



# ALUMINUM

## The Metal and Its Alloys

*(A Critical Descriptive Treatise)*

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DEDICATED TO  
MY MOTHER  
MRS. R. A. KORSUNSKY





## PREFACE

An author writing a book must justify its publication either by including material not existing elsewhere or by treating existing information in some original way. He must also strive to appeal to a definite audience.

The author of this volume has endeavored to comply with both of these specifications. The book is addressed to readers interested in aluminum, which means those connected with a foundry, rolling mill or a structural plant and those university students and professors who wish to broaden their knowledge in special branches of the technology of metals.

The author has endeavored to include only condensed material and such information as may be useful from the industrial viewpoint. It was his desire to awaken the critical power of the industrial mind and to furnish substantial information concerning various possibilities and innovations. Therefore the greater part of the book is devoted to the description of definite systems of binary and ternary alloys showing the fields of composition which are or may be used and the properties which can be obtained or expected from them. A large section of the description of each series is given to the so-called constitutional diagrams which present the changes in alloys resulting from variations in temperature.

Two variations are given for many of the diagrams and the purpose of this repetition is twofold: they show how the interpretation of a given series may differ and how reliable are the results from the standpoint of the practical man interested in the aluminum end of the diagram. The so-called "imaginary" diagrams included will no doubt call forth severe criticism, but the author justifies their inclusion because they relate to series which do not readily lend themselves to experi-

mental investigation, yet are too important to be ignored. Information already accumulated permits the making of such a prognosis in a number of cases.

The arrangement of the alloy descriptions corresponds in general to the alphabetical order of the second alloyed element in the table of chemical symbols and only in cases where a number of alloys form an evident natural group has the order been shifted to avoid repetition and to stress their similarity.

The diagrams of mechanical and other physical properties, with explanations, form a large portion of the descriptive material. In these sections we have tried to show the relationship between properties and composition in a continuous way, *i.e.*, by graphs. The celluloid square with abscissa and co-ordinates is to permit the reader to obtain easily and quickly the value of a property corresponding to a given composition, or the reverse. This is somewhat of an innovation which it is hoped will meet with the approval of the reader.

Chapters dealing with the corrosion resistance of aluminum and with the "Structurography" of the aluminum alloys were written mainly on the basis of the author's own investigations. The word "Structurography" is newly introduced by the author in a substitution for the usual term "metallography." The latter term is too broad to be applied to structural descriptions, while the term "micrography" is too narrow and does not cover macrography.

Tables illustrating the most generally used compositions of cast and wrought alloys and their properties are also a part of the book as well as a general table of the properties of the metal itself.

It is the purpose of the author to give throughout in condensed form only information giving insight into foundry and rolling mill methods, omitting irrelevant data and minor and unimportant details. The promotion of general knowledge and critical thought is his chief aim and if he has succeeded in clarifying the theory and practice of aluminum metallurgy

in the minds of the reader he will feel that the volume has accomplished its purpose.

The author desires to express his gratitude and appreciation to the following for their generous assistance and aid in preparing the manuscript for publication: —

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## ABBREVIATIONS USED IN THE DIAGRAMS OF CONSTITUTION AND PHYSICAL PROPERTIES

### I. To denote constitution:

- liq.* — the liquid phase
- (Al-Me) a solid solution of the element Me in aluminum.
- (Me-Al) a solid solution of Al in the element Me.
- $(Al_x Me_y + Me)$   
(Al) } means a solid solution of either Me or Al  
in a compound  $(Al_x Me_y)$

### II. To denote state:

- c.* as cast
- s.c.* " sand cast
- c.c.* " chill cast
- f.f.* " furnace frozen
- f.c.* " furnace cooled
- a.* " annealed
- an-d.* " "
- c. a.* " cast and annealed
- q.* " quenched
- c.q.* " cast and quenched
- s.c.q.* " sand cast and quenched
- ag.* " aged
- q. ag.* " quenched and aged
- r.* " rolled
- dr.* " drawn
- c.r.* " cold rolled
- h.r.* " hot rolled
- h.f.* " hot forged
- extr.* " extruded
- r.a.* " rolled and annealed
- h.r.s.* " hard rolled sheet
- h.dr.w.* " " drawn wire
- f.an.* " fully annealed
- t.* " tempered
- h t.* " heat treated
- q.t.* " quenched and tempered

### III. To denote property:

- T.S.* Ultimate Tensile Strength
- EL.L.* Elastic limit
- P. l.* Proportionality limit



<i>Y.P.</i>	Yield point
<i>El.</i>	Elongation
<i>A.R.</i>	Area reduction
<i>Imp.</i>	Impact resistance
<i>Imp. Ch.</i>	Impact Charpy test
<i>Iz.</i>	Izod test
<i>E.R.</i>	Electric resistivity
<i>E.C.</i>	Electric conductivity
<i>a</i>	Temp. factor of <i>E.R.</i>
<i>E.M.F.</i>	Electromotive force of dissolution
<i>T.E.P.</i>	Termo-electric power
<i>Br.</i>	Brinell hardness obtained with the load / <i>ball diam</i> <sup>2</sup> ratio = 10.
<i>Br.P/d</i>	means Brinell hardness obtained under a load ( <i>P</i> ) and a ball diameter ( <i>d</i> )
<i>Sh.Un.</i>	Shore hardness universal hammer
<i>Sh.Mg.</i>	Shore hardness magnifier hammer
<i>H.C.</i>	Heat conductivity
<i>V.C.</i>	Volume change (cubic expansion)
<i>T.H.</i>	Total heat capacity

**PART I**  
**PROPERTIES OF METALLIC ALUMINUM**



## PROPERTIES OF METALLIC ALUMINUM

ALUMINUM crystallizes in the cubic system. Its crystalline lattice consists of face-centered cubes with an edge  $4.07 \text{ \AA}$ <sup>1</sup> long and minimum atomic distances of  $2.88 \text{ \AA}$ . This lattice is apt to develop cleavage surfaces along the three most important directions of the cubic system — the octahedral, hexahedral and the rhombo-dodecahedral planes. The method of producing large sized crystals of aluminum for experimental purposes consists in annealing the samples of the purest cold-worked metal "as delivered" for 6 hours at  $550^\circ$ , straining them by tension until a total elongation of about 1.6% in 2 inches is produced (critical strain) and annealing the strained pieces for 4 or 5 days, gradually increasing the temperature from  $300^\circ$  to  $600^\circ \text{ C}$ . Test pieces with monocrystalline cross-section obtained in this way show that the inherent strength of the aluminum crystals is about 9000 pounds per square inch with an elongation of 80%. The properties of the different surfaces were studied by O'Neil, who found their Brinell hardnesses to differ quite sensibly. These and all other properties of aluminum, as investigated up to the present, are reproduced in Table 1, both for the purest form of the metal (less than .5% impurities) and for the average commercial metal with 1.5% of contamination.

To make aluminum commercially useful one has to begin by remelting the ingots delivered from the electrolytic plant and casting the metal into ingots to be rolled. Aluminum, either pure or slightly contaminated, undergoes the process of crystallization in a very unfavorable way in that it builds up large grains of non-uniform size with impurities segregated in comparatively large masses, and therefore the metal cannot be used in the cast state unless sufficiently alloyed. Only ingots and billets to be worked by rolling, pressing, extruding or tube drawing are produced by casting.

<sup>1</sup> An.  $\text{\AA}$ engström is equal to  $10^{-8} \text{ mm}$ .

Melting may be done either in open hearth furnaces or in crucibles. The first method is the better, provided the inside of the furnace is lined with closely fitting fireclay brick. Weak bricks like silica, and those which are apt to crack on cooling, like magnesia or dolomite, are not suitable. The difficulty with aluminum is that its specific weight is not much different from that of the refractory material and its viscosity is quite pronounced; hence broken pieces of lining may become entangled in the aluminum and remain there until they pass into the ingots, thus spoiling large quantities of metal.

For crucible melting, large graphite-clay pots, fixed within the shells of tilting furnaces, are the best. Such crucibles withstand a large number of heats without deterioration and no mechanical contamination of the ingot metal results. Fireclay crucibles are not used for melting aluminum as they are not sufficiently strong, while iron crucibles are liable to contaminate aluminum and to lower its general grade.

Very contradictory opinions are held by the practical manufacturers and also by some scientific men concerning the material of which the vessels for aluminum melting should be made. It is frequently stated that crucibles of natural graphite, or of pure graphitized carbon are apt to cause the formation of aluminum carbide, while clay crucibles were supposed to allow their silica to be reduced to silicon, the latter dissolving in the aluminum. Finally, iron pots might probably introduce iron into the aluminum. At present we know that no actual interaction between aluminum and carbon or silica starts before the aluminum is heated to  $1200^{\circ}\text{C}$ , which practically never happens in the foundry. We also know that no substantial amount of the iron is dissolved unless aluminum and the iron pot are heated above  $800^{\circ}\text{C}$ . The latter may, of course, happen quite frequently; nevertheless, it may be stated positively that the nature of the vessel is of secondary importance, while its cleanliness and lack of deterioration are the main factors to be considered.

The temperature which the molten aluminum is permitted to reach, the time during which it is exposed to this tempera-

ture, and finally the temperature of casting have always been considered to exert a great influence upon the final properties of the metal. This opinion is undoubtedly true to facts in regard to finished castings, but is extremely doubtful as to metal intended for rolling. In 1922, Rosenhain succeeded in showing that neither the temperature of the furnace nor the temperature of casting the ingots has much effect on the production of a sound and uniformly strong finished product; even when the metal is heated to 1100° and cast at 900°, the properties do not differ much from those obtained with a much more careful melting.

On the other hand, the crystal growth in the ingot metal is undoubtedly influenced by the temperature of casting. Therefore, the first operation of breaking down and the immediately following operations of rolling may not go with equal smoothness if the metal is cast indiscriminately. For that reason, every mill has to enforce a certain rule for the heating and pouring temperatures. The lower the temperature of melting, the less the final shrinkage, the smaller the pipe scrap, and the lower are the expenses of the melting itself. Therefore the adoption of the lowest possible temperature for casting is of great advantage.

The action of gases upon aluminum was considered to be very strongly detrimental until the latest investigations by Czochralsky. He found by blowing different gases through molten aluminum, that only a very slight occlusion occurred at the temperatures at which aluminum is regularly held in a furnace. An actual gas occlusion does not occur below 900° and only above 1100° does it become seriously destructive to the properties of aluminum. He made his investigation by studying the specific weights of the furnace-cooled samples, from which he deduced the porosity and the corresponding amount of occluded gas (Fig. 1). Of course, a certain amount of gas does not become occluded, but forms compounds with aluminum. Czochralsky found, however, that the latter do not seriously affect the final properties of the rolled metal, as practically all impurities formed in this way segregate in the

upper part of the metal. Carbon dioxide, hydrogen and sulphur dioxide were found to be the most readily absorbed gases, nitrogen and air the least occluded while oxygen and carbon dioxide take an intermediate position. Hydrogen and sulphur dioxide become occluded at much lower temperatures than the others, with the exception of carbon dioxide. The latter is occluded in moderate amount, but the absorption begins in the very neighborhood of the melting point.

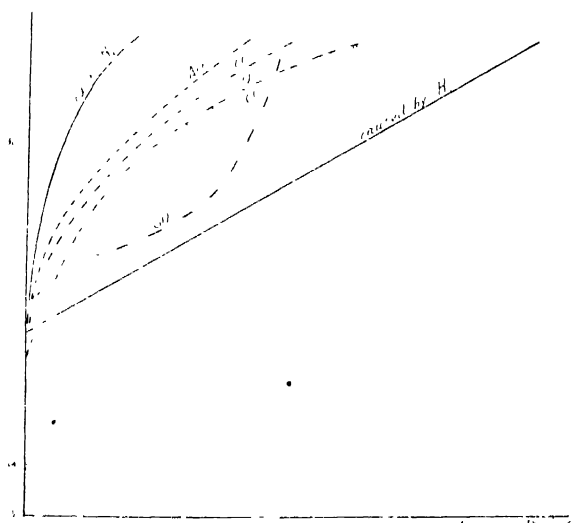


FIG. 1. Porosity caused by gas absorption in aluminum  
Czocharski (Z. Metallkunde, 1922, p. 217.)

In aluminum melting practice, gas does not bubble through aluminum and the metal does not have to be agitated by stirring; hence, not very much gas occlusion can occur, and by melting aluminum in large graphite crucibles in a tilting furnace, gas occlusions can be considered as entirely eliminated. With the open-hearth furnace, the use of sulphur-free fuel and of a slightly reducing atmosphere helps to give the same results.

Aluminum ingots, as cast, are of very different sizes. The ductility of metallic aluminum is so great that very heavy passes can be adopted, particularly in the hot state, and a

large amount of cold work can be done on the metal. The rolling schedules differ widely; one example is given here as an illustration.

<i>Ingot Sizes</i>	<i>American</i>	<i>German</i>
Length	24"	21"
Width	13"	8.5"
Thickness	2"	4.5"
Weight	60 lbs.	78 lbs.

Mills used. 30 x 120, 28 x 84, 28 x 36 in.

Speed of hot rolling, 200 to 300 ft. per min. at 400 to 500° C.

Speed of cold rolling 120 to 200 ft. per min.

Number of ingots per operation, 25 to 50.

Breaking down hot:

<i>For 24" Sheets</i>			<i>For 36" Sheets</i>		
<i>Pass</i>	<i>Lengthwise</i>	<i>Crosswise</i>	<i>Pass</i>	<i>Lengthwise</i>	<i>Crosswise</i>
	in.	in.		in.	in.
1	2 — 1½		1	2 — 1½	
2		1½ — 1⅛	2		1½ — 1⅛
3		1⅛ — 7/8	3		1⅛ — 7/8
4	7/8 — 5/8		4		7/8 — 9/16
5	5/8 — 3/8		5	9/16 — 1/2	
6	3/8 — 1/4		6	1/2 — 3/8	
			7	3/8 — 1/4	

(In the German practice hot rolling stops at a thickness of 10 m/m.)

Roughing: Cold in 6 to 12 passes down to 0.125 or 0.095 in.

Annealing: at 480° for 1 hour.

Pack rolling: 2 to 8 sheets in a pack, down to 36 B & S gage.

Finishing and straightening: 25 to 30 passes.

Annealing is a very important part of the process in an aluminum rolling mill. It is said that in many mills each anneal lasts for almost 24 hours at a temperature of 450°. This statement appears somewhat doubtful as such a method would lead to waste of fuel and time and to high overhead expenses. It is probable that the majority of mills use shorter anneals, lasting not over 2 or 3 hours, and even this length of time is not actually necessary. H. Roerig (Z. Met., 1924, p. 267) and Wetzel (Z. Met., 1924, p. 65) ascertained the strength, ductility and the grain sizes obtainable by different treatments, *i.e.*, by annealing at different temperatures, for different times, and in different media (Figs. 2a, b, c, d). A



very short immersion (less than 1 min.) of aluminum sheets or wire in a fused mixture of sodium nitrate and nitrite held at  $400^{\circ}$  gives enough ductility to permit a considerable amount of cold work. The same authors found that heavy passes are best able to produce uniformly refined grains, and that if the last finishing operation consisted in 90% reduction with rolls of small diameter and with packs of two to four sheets per pack

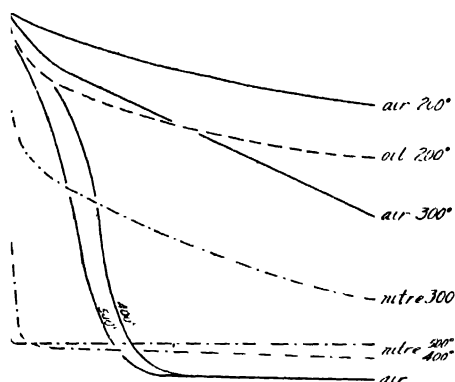


FIG. 2a. The process of annealing rolled aluminum sheet.  
By N. Rochrig (Z. Met., 1924, p. 267).  
Change in ult. str. in the first 5 min.

a subsequent annealing anywhere from  $500^{\circ}$  to  $600^{\circ}$  and from five minutes to two hours will not cause excessive growth of grain. The grains in the finished product should not be below 0.03 mm. for material to be used as sheets and not over 0.10 mm. in metal intended for stamping and spinning. Grains smaller than 0.03 mm. can be allowed only in cold-rolled stock. The spatial recrystallization diagram for a 99% pure rolled aluminum, which shows the grain size in its relationship to the amount of cold work and the temperature of annealing, is given in Fig. 3.

The chemical resistivity of aluminum is of great importance

# PROPERTIES OF METALLIC ALUMINUM

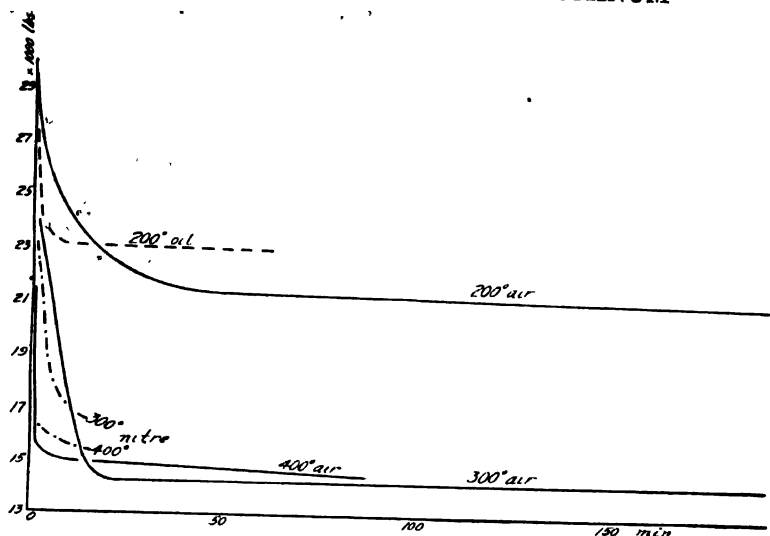


FIG. 2b. The process of annealing rolled aluminum sheet  
By N. Roehrig (Z. Met., 1924, p. 267).  
Change in ult. str. in three hours.

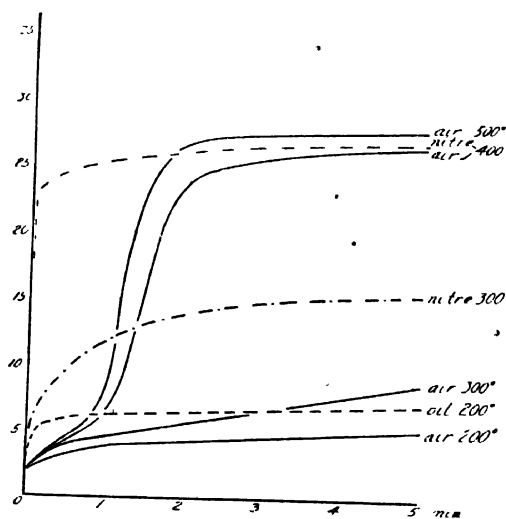


FIG. 2c. The process of annealing rolled aluminum sheet.  
By N. Roehrig (Z. Met., 1924, p. 267).  
Change in ductility in the first 5 min.  
(L = 11.3 f.)

and a quick method for its determination is desirable. One such was suggested by Mylius (Zeit. fuer Metallkunde, 1922, p. 233). It consists in immersing a suitable sized piece of the metal in a test tube containing a 10% (by weight) solution of hydrochloride acid, and observing the rise in temperature.

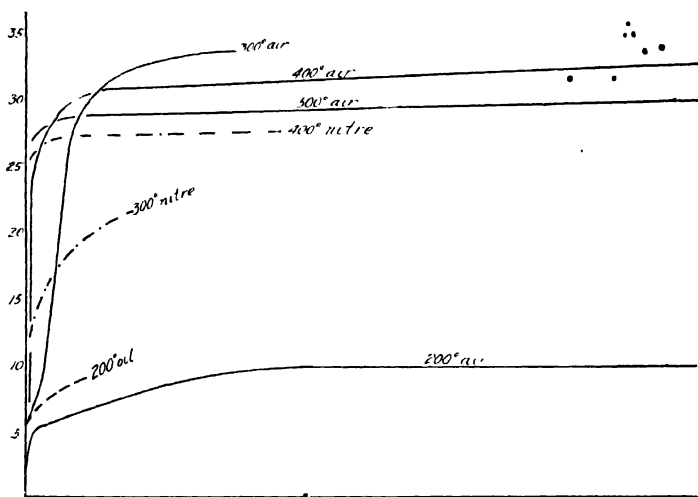


FIG. 2d. The process of annealing rolled aluminum sheet. By N. Roehrig (Z. Met., 1924, p. 267). Change in ductility in three hours.

The rapidity of this rise shows the chemical resistivity and gives the class of the tested material; A suggested classification is given in the table below.<sup>1</sup>

Class	Rate of Increase in Temperature			
Ia	Less than 1° C. per minute			
Ib	1 to 4°	"	"	"
IIa	4 " 7°	"	"	"
IIb	7 " 10°	"	"	"
III	10 " 20°	"	"	"
IV	More than 20°	"	"	"

The limits of strength and ductility in a reasonably strong cold-worked aluminum, and in such annealed under the best conditions, are not definitely known. The curve showing the relationship of strength and ductility (elongation in 2") has the form given in Fig. 4. With too heavy a cold work both

<sup>1</sup> For further details see the chapter on the chemical stability of aluminum alloys (Aluminum and Corrosion).

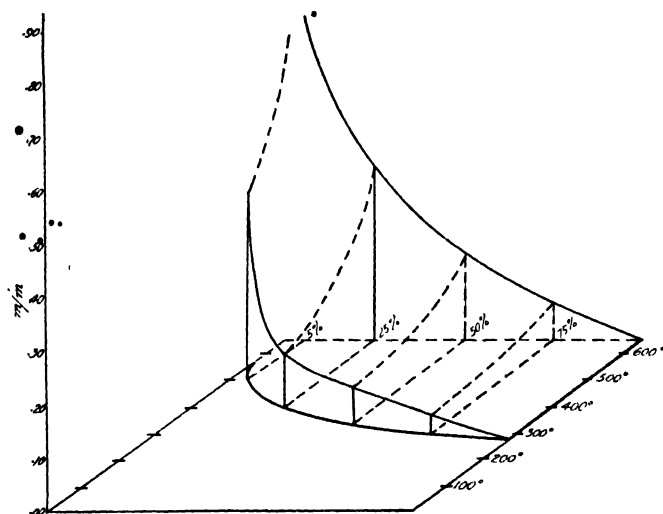


FIG. 3. Recrystallization diagram for 98.5% aluminum sheet metal. It permits to find the temperature at which new grains start to form, following a given amount of cold reduction, and the grainsize obtainable by annealing for  $\frac{1}{2}$ -2 h. at the chosen temperature.

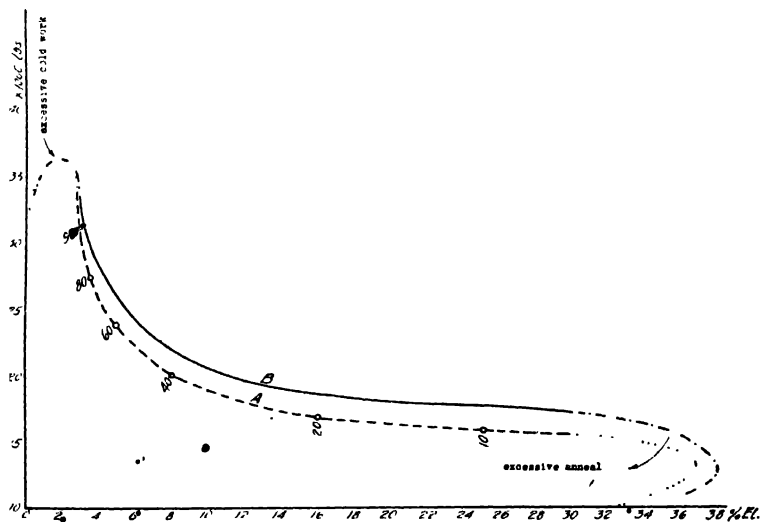


FIG. 4. Strength-Elongation curves. A for rolled sheets; B for extruded and roll-finished rods. Figures below curve A show per cent of reduction in rolling.

strength and ductility diminish owing to the separation of the metallic grains long before they are distorted to the limit. With slightly less cold work we find the highest strength and a reasonable minimum of ductility. Partial cold work or a partial anneal results in strengths and ductilities shown in the central and larger part of the curve. With no cold work, or with the best possible annealing, we get an acceptable minimum of strength and the maximum of ductility. With an over anneal we find an excessive growth of grains and a coagulation of intergranular impurities along very rough boundaries; in this condition the metal is "burned" and both strength and ductility are impaired.

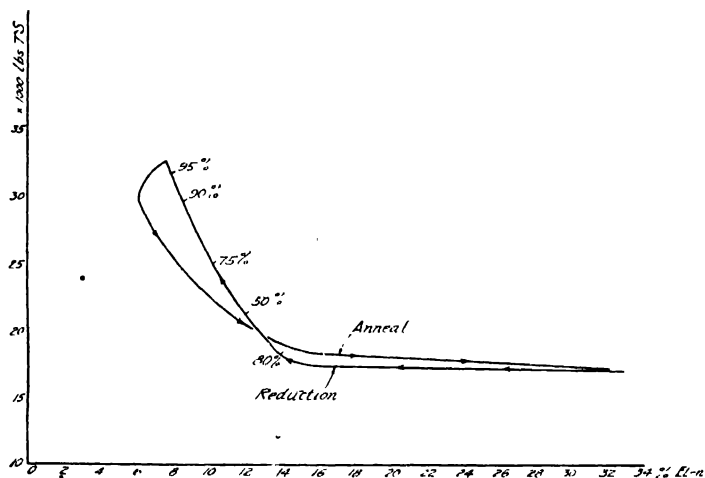


FIG. 4a. Strength-Elongation diagram for aluminum (99.5%) wire for  $d = 0.080-0.500$ " range  
figures show % area reduction by drawing.

The central part of this curve may be supposed with fair approximation to represent such hyperbolic equations as are shown in Sec. 50 of our table of physical properties. These equations allow us to calculate with a reasonable degree of accuracy the corresponding values of strength and ductility.

Fig. 4a represents the relationship of strength to ductility in aluminum wire.

In connection with the properties of pure aluminum as compiled in Table 1, the following explanations are desirable:

Secs. 2, 3, 10 and 19: The values of the physical features are given in round figures which must be divided by  $10^6$  to obtain the actual magnitudes.

Secs. 23 and 25: the figures must be multiplied by  $10^6$ .

Sec. 8, the transformation point: a number of authors consider aluminum as a metal with an allotropic modification, and the temperature of transformation is given as located about  $565^\circ$ . Others believe that no real transformation occurs in aluminum but simply that an aluminum-silicon eutectic shows a stop in the cooling curves. This is not a very satisfactory explanation as silicon is now known to stay in solid solution at least up to a content of 0.70% at the usual rates of cooling, and no eutectic melting temperature can be observed for solid solutions.

Sec. 10, Thermal conductivity: This represents the amount of heat in gram-calories which will flow through a 1-cm cube in one second if the difference in temperature of opposite faces is  $1^\circ \text{C.}$ , at the corresponding temperatures.

Sec. 41, Fatigue formula: By this formula we can find the number of reversals which the metal will withstand at any given stress. By modifying this formula we can find the value of the stress which could be withstood for at least 20 million reversals, representing practically the extreme conditions of fatigue that can occur in practice. The corresponding stress for aluminum is approximately 7000 lbs. per inch.

Secs. 39 and 40: Impact resistance of aluminum and of its alloys, has never been studied in a sufficiently systematic way, and no attempt has been made to standardize the method of investigating this feature, or to find a relationship which would permit even a rough comparison of figures obtained by the Izod, Charpy, and other tests.

Sec. 45, Point of self-annealing: Prolonged experiments by Professor Carpenter and his co-workers have shown that hard-worked aluminum suffers about 30% decrease in strength in the course of years if its temperature is kept somewhere over

100°. This decrease in strength is not accompanied however by a visible grain growth and for practical purposes the latter can be considered as taking place between 150 and 200°C.

Sec. 46: The recrystallization temperature is the point at which elongation increases and strength decreases practically instantaneously as soon as this point is reached, and a forma-

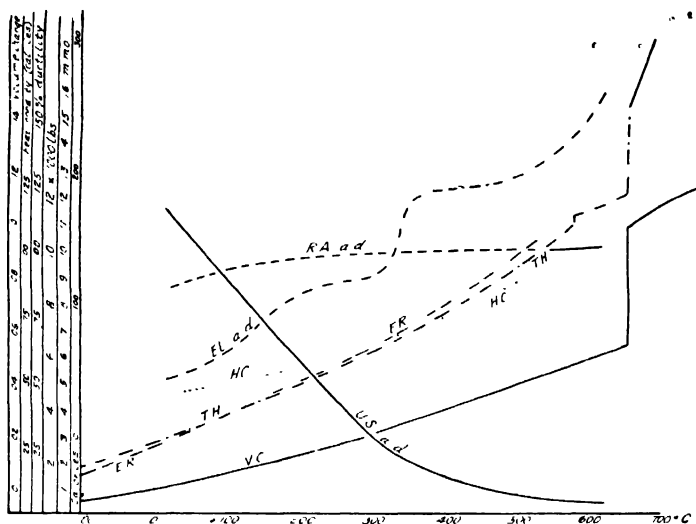


FIG. 5. Effects of temperature upon the physical properties of pure commercial aluminum.

tion of new grains can be observed quite shortly thereafter. This temperature lies between 300 and 330°C.

The effects of temperature upon different physical properties of a good grade (over 99.5%) rolled and annealed aluminum are shown in Fig. 5.





TABLE I. — PROPERTIES OF PURE ALUMINUM

	<i>Purest</i>	<i>Commercial</i>	<i>Remarks</i>
1. Specific gravity	<i>Over</i> 99 5 $\frac{5}{6}$ $\frac{2\ 68}{s.c.}; \frac{2\ 70}{c.r.}$	<i>Over</i> 98.5 $\frac{5}{6}$	
2. Thermal expansion ( $10^6$ )	$\frac{24\ 5}{an.}; \frac{24\ 30}{h.r.}$		Brislee (1911. Tr. Far. Soc. 221)
3. Thermal exp. formula ( $10^6$ )	(23 54 + 0.34T)*		*Dittenberger (1902. Z.d., V.D.I. 1532) Greenwood (Proc. Ro. Soc. 1909. 396)
4. Boiling temperature	1830 + 50° C.		*Richards (Met. Calc. S Calculated figure)
5. Heat of ebullition	61500 Cal*		*U.S.B.S.
6. Melting temperature	658 7C	64 Cal*	*Lashtshenko (1914 J.R.P.S. 371)
7. Heat of fusion	565° C*		*Lashtshenko (loc. cit.)
8. Transformation temperature?	5 Cal.*		*
9. Heat of transformation?	524*		*Lees (Phil. Trans. 1908. 208)
10. Thermal conductivity	$\frac{2143}{18^{\circ}}; \frac{2228}{100^{\circ}}$	*470	*Jaeger (1900 T. E.F. Wiss. Abh.)
11. Spec. heat factor			
12. Spec. heat formula at normal temperature	2024 + 0.0023 t.*		*Brislee (1911 Tr. Far. Soc.)

# PROPERTIES OF PURE ALUMINUM — Continued

	Purest Over 99.5% 187 Cal.*	Commercial Over 98.5%	Remarks
13. Total heat at melt. p.			*Lastshenko (loc. cit.)
14. Electric resistivity ( $10^6$ )	$\frac{2.65^* - 2.8^{**}}{\text{c.dr.} \ \& \ 20^\circ}$	3.06***	*Richards & Thompson (1897 J. Fr. M. 195)** B. S. Sc. P. 148
15. Temperature factor	+ .0039 ( $0^\circ - 100^\circ$ )		Average of various data
16. High temp. conductivity	$\frac{3.86}{100^\circ}; \frac{5.17}{200^\circ}; \frac{6.56}{300^\circ}; \frac{8.00^*}{400^\circ}$		*Nicolai (1907)
17. Annealing factor	+ .01*		*Richards + Thomps.
18. Magn. susceptibility ( $10^6$ )	65	$\frac{.695}{20^\circ}; \frac{60^*}{657^\circ}$	Honda (1910 An. d. Ph. 1027)
19. Thermo-el power ( $10^6$ ) volts	$\frac{\text{Al}}{\text{Cu}} = \frac{4.51 - .0244t}{.00013t^2}$		Northrup (191-7 Ch. & Met.)
20. Light adsorption ind.	$\frac{2.85}{431} - \frac{3.92}{656 \text{ microns}}$		*In the visible spectrum
21. Light refract. ind.	$\frac{0.80}{431} - \frac{1.50}{656 \text{ microns}}$		*In the visible spectrum
22. Light reflexion power	74%		*In the visible spectrum
23. Mod. elast. in tension ( $10^6$ )	$\frac{9.34}{\text{cast}}; \frac{9.79}{\text{c.dr.}}; \frac{9.84}{\text{c.r.}}; \frac{10.67}{\text{f. an.}}$		*Averages of various figures

24. Temperature factor

25. Mod. elast. in torsion (10<sup>6</sup>)

26. Poisson's ratio

27. Temp. factor

28. Ult. strength lbs. inch<sup>2</sup>

" higher t-s

" "

29. Yield point lbs./in.<sup>2</sup>

30. Prop. limit lbs./in.<sup>2</sup>

31. Elongation %

"

"

-0.12% per 1° C\*

$\frac{3}{20} \frac{87}{100} ; \frac{3}{100} \frac{73}{200} ; \frac{48}{200} \frac{10}{300} ; \frac{2}{400} \frac{63}{400}$

0 36

$\frac{0.16\%}{1^{\circ}\text{C}}$

$\frac{11000 - 14500}{\text{cast } 700^{\circ}} ; \frac{35000}{\text{h.r.s.}} ; \frac{45000}{\text{h.d.w.}} ; \frac{15000}{\text{an.400}^{\circ}}$

$\frac{16000}{100^{\circ}} ; \frac{12000}{200^{\circ}}$  (med. hard metal)

$\frac{11200}{100^{\circ}} ; \frac{7500}{200^{\circ}} ; \frac{4000}{300^{\circ}} ; \frac{2000}{400^{\circ}} ; \frac{2000}{400^{\circ}}$  (f. an.)

$\frac{6000}{\text{cast}} ; \frac{25000}{\text{h.r.s.}} ; \frac{33000}{\text{h.d.w.}} ; \frac{8000}{\text{an.400}^{\circ}}$

$\frac{3000}{\text{an.}}$

$\frac{33}{\text{cast}} \frac{0}{\text{c.r.}} ; \frac{2-5}{\text{an.400}^{\circ}} ; \frac{40}{\text{an.400}^{\circ}} ; \frac{19}{\text{cast}} \frac{0}{700^{\circ}}$

25 0 (20-220°) med. hard

$\frac{45}{20^{\circ}} \frac{0}{82} - \frac{105}{300} \frac{0}{400-500}$

\*Koch and Dieterle (An. Ph. 1922)

Koch & Danneker (Ann. d. Ph. 1915, 197)

B. S. Circ. 76

B. S. Circ. 76

Ph. Prop. Mats. (B.S. Circ. 101)

Martin (J. Inst. Met. 1924. I 121)

Martin (J. Inst. Met. 1924. I 121)

Ph. Prop. of Mats. (B.S. Circ. 101)

Ph. Prop. of Mats. (B.S. Circ. 101)

Martin

Martin (loc. citus)

Martin

# ALUMINUM AND ITS ALLOYS

PROPERTIES OF PURE ALUMINUM — Continued

	Purest Over 99.5%	Commercial Over 98.5%	Remarks
32. Area contraction %	$\frac{30.0}{\text{cast}}; \frac{20.0}{\text{c.r.}}; \frac{40.0}{\text{f.c.d.}}; \frac{35.0}{\text{an.400}^\circ}$		(B.S. Circ. No. 101)
"	$\frac{65-75.0}{20^\circ-220^\circ}$ (med. hard)		Martin (loc. citus)
"	$\frac{70-95}{20^\circ-300^\circ}$ (an. 400°)		Martin
33. Hardness Brinell	$\frac{21-24}{\text{s.c.}}; \frac{22}{\text{f.f.}}; \frac{35}{\text{h.r.}}$	$\frac{30}{\text{s.c.}}$	Phys. Prop. Mats. (B.S. Circ. 101)
"	$\frac{28.3}{\text{O.I.}}; \frac{21.3}{\text{I.I.}}; \frac{20.6}{\text{O.I.}}$ (fully ann.-d.)*		*Hardness upon cryst. surfaces. O'Neill (J.I.Mat. 1923 (II))
34. Hardness by Meyer's formula	$P = \frac{23.5 \text{ d}^{1.39}}{\text{an-d}} = \frac{31.8 \text{ d}^{1.105}}{\text{h.r.}}$		O'Neill (J. Inst. Met. 1923 (II))
35. Shore Hardness magn. hammer	$\frac{3-4}{\text{s.c.}}; \frac{18-20}{\text{h.r.}}; \frac{4.5}{\text{an.400}^\circ}$	$\frac{5.0}{\text{c.c.}}$	Average of differ. figures.
36. Scratch Hardness	Unknown		
37. Ult. strength in compression		$\frac{67000}{\text{cast}}$	
38. Ult. strength in shear		$\frac{12000}{\text{cast}}; \frac{16000}{\text{m.h.r.}}$	Sargent (Proc. Am. S.T.M. 1920)



**PART II**  
**SYSTEMATIC DESCRIPTION OF ALUMINUM**  
**ALLOY SERIES**



## THE ALUMINUM-SILVER SERIES (Al-Ag)

MANY attempts have been made to use silver as an alloying element for aluminum. The constitutional diagram of this system was studied first by Petrenko (Z. an. Ch., vol. 46, p. 53, 1905) and afterwards was reinvestigated by Broniewski. Both authors pay much more attention to the chemical aspects of the constitutional diagram, i.e., the presence of compounds,

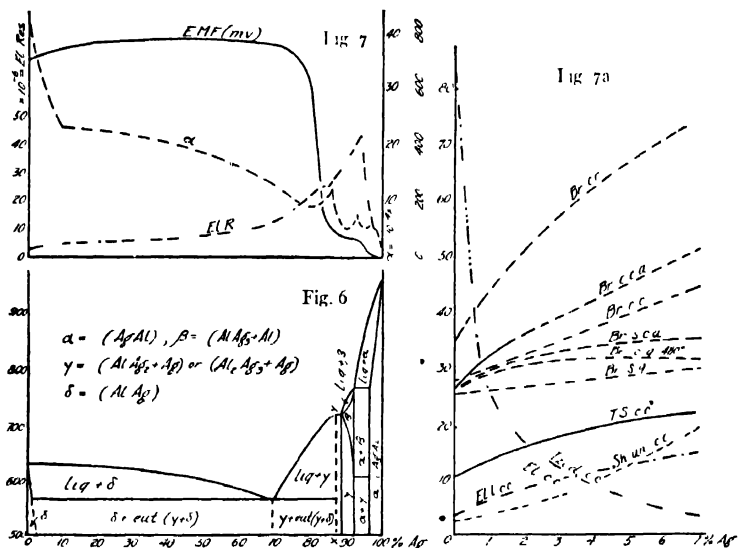


Fig. 6. Const-1 diagram of the Al-Ag series by Petrenko (Z. An. Ch. 1905, v. 46 p. 53). The line xy is drawn to represent the Al<sub>2</sub>Ag<sub>3</sub> composition according to Broniewski

Fig. 7. (above) Electrical properties of Al-Ag alloys.

Fig. 7a. Mech. properties of the Al-Ag alloys by Korsunsky.

than to the physical and mechanical properties and the structural details of the series. Due to the use of small quantities, not even their constitutional diagrams are fully reliable.

According to Petrenko two compounds are formed, AlAg<sub>2</sub> and AlAg<sub>3</sub>; while Broniewski insists on the presence of the compound Al<sub>2</sub>Ag<sub>3</sub> and the non-existence of AlAg<sub>2</sub> (Fig. 6).

Additions of silver to aluminum lower the melting temperature of the alloy very slightly, but continuously, and a eutectic



is formed at nearly 69% silver, composed of aluminum with one of the mentioned compounds. Neither of the authors indicates the presence of solid solutions at the aluminum corner of the diagram. The electrical properties and the hardness of the whole series of aluminum-silver alloys are given in Figs. 7 and 8.

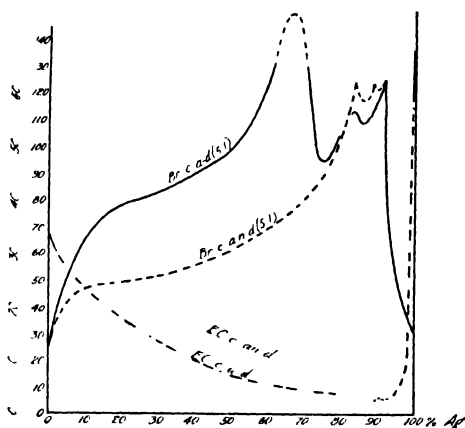


FIG. 8. Hardness and electric conductivity of the Al-Ag series in the annealed and quenched (after casting) state. Le Gries and Broniewski (Rev. Met., 1913)

The author's own experiments with a few aluminum-silver alloys at the aluminum end show that they have some remarkable properties. For example, comparing the Brinell hardness of the chill-cast or sand-cast metal (see Fig. 7a) with the hardness in the quenched and the annealed states, we find that quenching from a temperature of  $480^{\circ}\text{C}$ . reduces the hardness of the chill-cast alloys (evidently by releasing the internal strains of chill-casting) but increases slightly the hardness of the sand-cast metal, making sand-cast and chill-cast alloys practically identical in hardness. The annealed and furnace-cooled alloys, however, show a great increase in hardness in both cases, which can be explained by the assumption of a range of solid solutions at the aluminum end with a solubility limit decreasing at higher temperatures, analogous to many other binary alloys. In this case, a fully annealed specimen

should actually possess a higher hardness, caused by the presence of aluminum-dissolved silver, while in the quenched state the hardness is lowered by the precipitation of aluminum-silver compounds from the solid solution. This makes it impossible to improve the properties of aluminum-silver alloys by any other method than a plain anneal.

Aluminum-silver alloys are very ductile, as to rolling qualities, and roll-hot up to 15% silver. In the cold state, however, only 50% reduction by rolling can be given to an alloy with 3% silver and not more than 30% reduction with 6% silver. The ductility of aluminum-silver alloy remains quite high, even when the pure Ag<sub>2</sub>Al compound is formed; at least up to 50% silver the alloys can be easily reduced by cold hammering.

At the silver end the alloys are hot short, but can be cold worked up to 6% aluminum. They require, however, a prolonged anneal at a temperature not exceeding 500°. Neither their chemical resistivity nor workability are sufficient to be of value. The Brinell hardness of cold-rolled aluminum-silver alloys is quite high (Fig. 7a).

Aluminum-silver alloys cast well, but when fractured are apt to show tiny films of a black substance around the grain boundaries. The increase in strength afforded by silver in chill-cast alloys is approximately 30% higher than that obtainable with the same amount of copper. The chill-cast alloy has a considerable impact resistance which compares favorably with that of almost every other aluminum alloy (Fig. 7a).

According to Bronievsky's data, the addition of silver increases the electrochemical potential of aluminum by approximately 0.05 millivolt. In consequence it might be expected that aluminum-silver alloys will be much less stable chemically than other aluminum alloys in which the potential remains either constant or diminishes upon the addition of the alloying metal. Nevertheless, brief tests show that aluminum-silver alloys are well able to preserve their silvery lustre, which is certainly more brilliant than that of other aluminum-rich alloys. The alloys with silver are quite resilient and sonorous, at a content of 7% silver at least.

## THE ALUMINUM-GOLD SERIES (Al-Au)

The constitutional diagram of these alloys is represented in Fig. 9. The aluminum corner of it shows nothing of interest; aside from the fact that gold can never become a commercial alloying element for aluminum, there is no chance whatever that such an alloy would have valuable properties. We mention this diagram only because aluminum has a powerful influence upon the properties of metallic gold. As little as 1% of aluminum reduces the melting point of gold to  $550^{\circ}$  making it hot short and unsuitable for any kind of hot work. On the other hand, at about 78% gold and 22% aluminum we find a

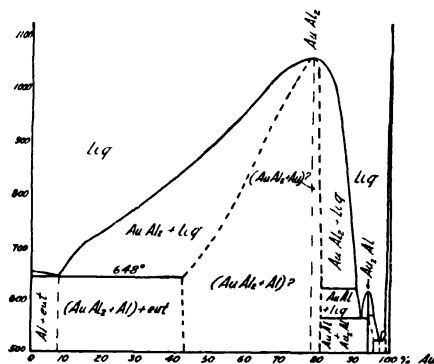


FIG. 9. Const. diagram of Aluminum-gold series by C. Heycock and F. Neville (Phil. Trans. 214 A)

definite compound  $\text{AuAl}_2$ , which melts at about the temperature of pure gold and seemingly is able to retain quite large amounts of either gold or aluminum, particularly the latter, in a state of solid solution. In spite of having a definite compound for their basis, alloys of this kind are apt to be sufficiently ductile and may possess some valuable properties as to color, chemical resistivity, hardness, etc. Unfortunately, no study of the physical or chemical properties of the system as a whole has yet been made; wherefore we can say nothing positive as to the chance of finding useful alloys somewhere in the central parts of the diagram.

## ALUMINUM-BORON SERIES (Al-B)

Here the conditions seem to be much less complicated than, for instance, in the aluminum-carbon system. Belonging to the same group of elements, aluminum and boron may be supposed to have a certain tendency to form solid solutions and little or no power to form compounds. In general, the conditions here might be compared with the aluminum-silicon and aluminum-beryllium systems with the difference that the amount of aluminum which can be dissolved in solid boron seems to be larger than in the other two elements, and that the eutectic point more nearly coincides with pure aluminum than it does even in the aluminum-beryllium system.

Investigators who prepared alloys of aluminum, very high in boron, at the temperature of the electric arc, found that besides a certain amount of free aluminum, the alloys show the presence of individual crystals of a different degree of transparency and either colorless or colored from yellow to deep scarlet. These individual crystals are now assumed to represent non-combined boron in the different stages of saturation with aluminum. According to some authors, about 17% aluminum by weight can be supposed to go into solid solution in boron.

The mentioned conditions are represented in the imaginary diagram in Fig. 10, where the most probable boundaries are shown in heavy lines. However, certain authors have noticed, at lower contents of boron, the appearance of a different kind of crystals, also uniform micrographically, which are assumed to represent the compound  $AlB_2$ . Some metallographical theorists refuse to acknowledge the existence of the compound  $AlB_2$  simply because aluminum and boron are too near each other in the periodic system. This theory may not agree with the facts; to show the different opinions graphically, we represent the following conditions by the dotted lines of our diagram. Somewhere near  $2000^\circ$  we assume aluminum to combine with boron, forming the compound  $AlB_2$ , which may retain a certain amount of both aluminum and boron in its

lattice. This phase may not be entirely stable and liable to dissociate at some lower temperature in a eutectoidal way leaving liquid aluminum (saturated with boron) and crystals of boron saturated with aluminum. Accordingly, in quickly cooled alloys with a boron content somewhere between 45 and 50%, we might be able to observe the phase  $AlB_2$ , while in slowly cooled alloys it may be absent.

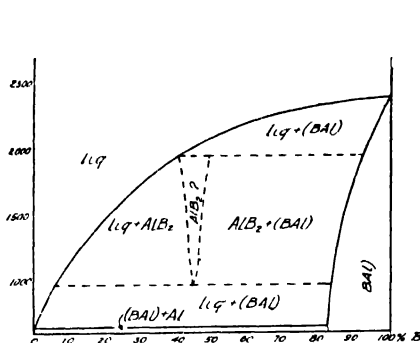


FIG 10 Imaginary const-l diagram for the Aluminum-Boron series.

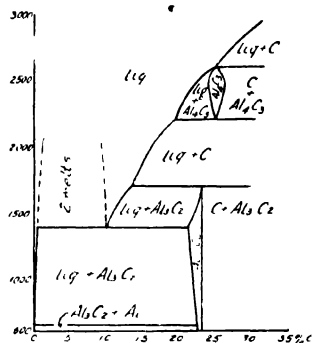


FIG 11 Imaginary const-l diagram for the Aluminum-Carbon series.

The aluminum-boron system can scarcely have any technical importance by itself, but a faint probability exists that boron may help to clean aluminum from gases by combining with nitrogen and oxygen and forming a more or less fluid slag of borates on the surface of the molten metal.<sup>1</sup>

#### THE ALUMINUM BARIUM AND ALUMINUM-STRONTIUM SERIES (Al-Ba, Sr)

No work of any kind has been done with alloys in this group and it seems futile to draw any opinion as to the constitution and properties of such alloys, because there is little chance of obtaining alloys with sufficient chemical stability and cheap enough to be useful. It is possible that slight amounts of barium and strontium may alloy with aluminum to form solid solutions with a varying limit of solubility and

<sup>1</sup> See Appendix.

therefore just as amenable to heat treatment as the aluminum magnesium alloys. On the other hand, these systems might be analogous to aluminum-calcium and have practically no industrial value at any amount of the alloying metal; finally, both may refuse completely to alloy with aluminum in the liquid state, as do the alkaline metals, sodium and calcium.

### THE ALUMINUM-BERYLLIUM SERIES (Al-Be)

The constitutional diagram of this system (Fig. 12) as developed by G. Oesterheld (Z. An. Che., 1916, vol. 97, p. 1) is quite analogous to that of aluminum-silicon but for the fact that the eutectic composition is located at 644° C. and at about 1.5% beryllium by weight. The investigator did not,

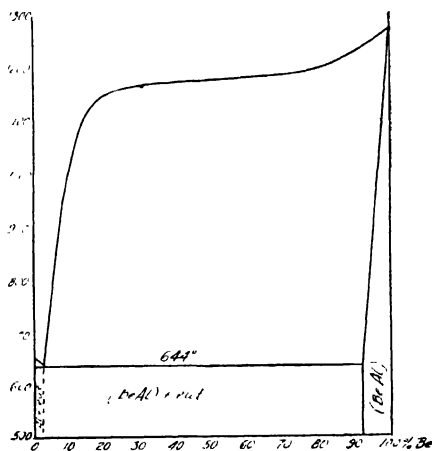


FIG. 12. Const-l diagram for Al-Be alloys by G. Oesterheld.

(Z. Anorg. Ch. v. 97, p. 1, 1916.)

however, subject the aluminum corner of the diagram to sufficient study and his findings can only be considered as preliminary inasmuch as he operated with a few grams of the melt in every case. We can hardly accept the mentioned eutectic point as positively identified, nor can we feel sure that

beryllium actually does not remain in a solid solution in aluminum to any measurable extent, as the investigator believes.

This system is greatly in need of a thorough investigation, particularly in view of the fact that two patents have been issued in the United States in which beryllium was mentioned as the only alloying element, and its amount was specified between 1 and 20% by weight and even up to 60%. Aluminum and beryllium both being ductile, there is a good chance that the eutectic or even highly supereutectic alloys with a large excess of beryllium might prove to have valuable mechanical and chemical properties similar or even superior to those of the aluminum-silicon system. The only drawback of these alloys would lie in their high melting and pouring points, assuming the liquidus curve of the diagram to be valid. At say 10% beryllium, the alloy would have to be cast at about 1050 to 1100°C. which would promote a burning of aluminum and introduce films of aluminum oxide in the casting, while the long interval of solidification and the difference in specific gravity might cause excessive segregation. These arguments point particularly to the necessity of a real investigation of the crystallization conditions in the high-aluminum part of the diagram, and of the properties of the corresponding alloys.<sup>1</sup>

#### ALUMINUM-BISMUTH, ALUMINUM-CADMIUM AND ALUMINUM-LEAD SERIES (Al-Bi, Cd, Pb)

Aluminum shows a strong tendency not to form homogeneous liquid alloys with metals whose melting point lies far below its own. Therefore, if bismuth, cadmium or lead are introduced into aluminum in substantial amounts (over 4%) they segregate at the bottom and form a separate layer (Figs. 13, 14, 15). The melting point of the aluminum resting above this heavy layer is slightly reduced by the presence of the latter; still the actual solubility of these metals in liquid aluminum is almost negligible even at a temperature of about 800°C.

<sup>1</sup> See Appendix.

If, however, only a small amount of any one of these metals is introduced into aluminum, an emulsion of the oil-water type results and the alloy may freeze without any substantial segregation or in such manner that the liquid globules of lead, cadmium or bismuth remain entangled in the mass of solid aluminum and are fairly uniformly distributed among the grains of the main metal. Here is the reason why a number of patents can mention these metals as components of different aluminum alloys. Lead is mentioned in two, cadmium in three and bismuth in two U. S. Patents. In no case, however, do we find an explanation as to how these particular additions are believed to influence the properties of the patented alloys.

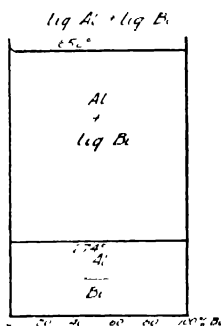


FIG 13.

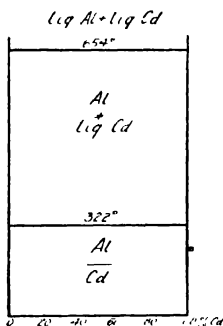


FIG 14.

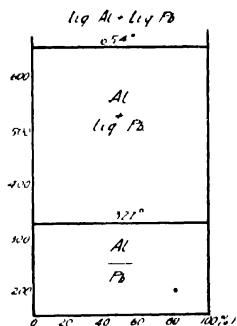


FIG 15

Const-t diagrams for the systems

Al-Pb by Gwyer (Z An Ch, 1008, p 147).

Al-Cd " " ( " " " " " p 149)

• Al-Bi " " ( " " " 1006, v 40, p 316)

There is no information whatever in the literature concerning the influence these three metals exert upon any mechanical property of cast aluminum. As to the worked alloys, we know that no one of the three addition metals is harmful in the rolling process if the latter is done cold. In hot work, bismuth is the most undesirable impurity. It does not affect aluminum in the same way as it acts upon copper because it forms no eutectics, but remains distributed in the form of tiny globules. An examination of rolled and annealed alloys showed that none of these metals has up to say 5% any



measurable influence upon either the ultimate strength or the ductility of aluminum.

Cadmium and bismuth, however, exert a certain refining action upon the grains of chill-cast aluminum and prevent almost completely the formation of columnar crystals and of coarse fractures. Aside from this unimportant feature, there is hardly any direction in which lead, cadmium or bismuth might act advantageously.

The chemical influence of slight additions of lead, cadmium and bismuth is also entirely unknown. In amounts of about 3 to 4%, cadmium and bismuth make aluminum very susceptible even to the action of tapwater, bismuth being worse than cadmium in this respect.

It may be worth while mentioning that H. Pecheux, one of the earliest users of the pyrometrical method of studying alloy systems, claimed (C. R. 1904) to have observed a decided rise in the melting point of aluminum, due to the presence of lead ( $32^\circ$  at 6% Pb), and bismuth ( $94^\circ$  at 25% Bi). And though these findings were not very reliable, the conclusions of Gwyer, who traced the corresponding constitutional diagrams, were also never re-examined and corroborated. Therefore a renewed study of these three systems is highly desirable.

Most recently the effects of an addition of cadmium to aluminum-zinc alloys were studied quite extensively. It was found that cadmium has no positive value in such alloys, any substantial amount of cadmium tending to lower their mechanical properties.

#### ALUMINUM-CARBON SERIES (Al-C)

The mutual relationship between aluminum and carbon has never been investigated in full, due to the almost insuperable difficulties. Nevertheless, the influence of carbon upon aluminum presents a very important question which has to be answered somehow. The opinion seems to prevail that any

carbon content is detrimental to aluminum and therefore many manufacturers hesitate to use either pure graphite or clay-graphite crucibles. On the other hand, while many experimenters and manufacturers hesitate to use even the clay-graphite crucibles when melting aluminum or its alloys at comparatively low temperatures, some others went as high as  $1200^{\circ}$  with pure graphite crucibles in their experiments and never observed a contamination of their alloys, in spite of using, for alloying elements, metals like nickel, cobalt, or silicon, all of which would be inclined to form compounds with carbon. Most recent experiments have shown that, while aluminum actually reacts with carbon, the product of the reaction forms a thin crust on the wall of the crucible and does not dissolve in aluminum. Even at the highest temperatures available in the foundries only a fraction of 1% of carbon dissolves in liquid aluminum and even this segregates and concentrates at the top of the cast ingot. Further, it was found that contaminated ingots, in which a content of carbon was established beyond doubt, do not show any noticeable deterioration of physical properties in the worked and annealed state.

Experiments at high temperatures have shown that aluminum combines with carbon either directly or indirectly, when one tries to reduce aluminum oxide with carbon, to form an aluminum carbide of the formula  $Al_4C_3$ , which has a limited stability both at very high temperatures (say over  $2600^{\circ}$ ) and at lower temperatures (approximately below  $2200^{\circ}$ ). Above and below these points we have a melt saturated with carbon, and solid carbon in graphite form. Micrographic investigations of alloys cooled quickly show that another carbide  $Al_3C_2$  is formed at lower temperatures and it is quite probable that this compound is the one present in aluminum that has been overheated in contact with carbon.

On the basis of the few facts known about aluminum-carbide, we can draw an imaginary constitutional diagram as given in Fig. 11. In it we assume that at temperatures above say  $2600^{\circ}$  more than 25% carbon can be dissolved in liquid aluminum (otherwise no molten pure carbide could be formed).

With any melt containing from about 20% to 25% aluminum, the compound  $\text{Al}_4\text{C}_3$  precipitates primarily in a temperature range of  $2200^\circ$  to  $2600^\circ$ . We assume that this compound dissociates at  $2200^\circ$  and that pure carbon crystallizes from liquids containing 13% to 19% carbon in the temperature range of  $1700^\circ$  to  $2200^\circ$ . Next, we assume that  $\text{Al}_4\text{C}_3$  precipitates primarily from any melt containing 0 to 13% carbon. There is an interval of say 0.05% to 19% carbon where, at temperatures about  $1400^\circ$  we have two immiscible liquids, one of the liquids representing mainly molten  $\text{Al}_4\text{C}_3$  which crystallizes en bloc and therefore completely separates from the melt. Below 0.5% carbon, aluminum carbide crystallizes primarily but can be compelled to remain within the liquid and to form a mechanically uniform solid alloy if chill-cast. Otherwise, under the conditions of slow cooling the carbide floats on the surface of the melt.

#### THE ALUMINUM-CALCIUM SERIES (Al-Ca)

The constitution of the system aluminum-calcium was studied by L. Donsky (Z. An. Org. Ch., 1908, volume 57, page 203). This investigator did not have in mind any technical application of his results and cared only for the establishing of the constitutional diagram. According to his diagram (Fig. 16) aluminum takes up calcium to about 8% when it forms an eutectic, freezing at  $610^\circ$ . With higher amounts of calcium, say about 33%, we get to the calcium-aluminum compound of the formula  $\text{CaAl}_3$ . This compound when liquid at  $692^\circ$  does not completely mix with the excess aluminum or calcium and thus two layers of liquids are formed. From 16 to 43% calcium, the freezing point of the compound remains unchanged, and only beyond these compositions the presence of excess metals causes a reduction of the freezing temperature down to the eutectic point on the aluminum side and to another at 75% calcium and  $550^\circ\text{C}$ . The investigator found no solid solutions at either the aluminum or the calcium

end of the diagram; according to him the alloys would represent: (1) primary grains of aluminum with an eutectic of  $\text{Al} + \text{CaAl}_3$  up to 8% calcium; (2) primary grains of  $\text{CaAl}_3$  with an eutectic mixture of the same two phases up to say 16% calcium; (3) a separate layer of  $\text{CaAl}_3$  plus primary grains of the same compound in an eutectic mass up to 33% calcium; (4) the pure compound  $\text{Al}_3\text{Ca}$ ; (5) a separate layer of  $\text{CaAl}_3$  plus primary grains of the same compound in an eutectic of aluminum and calcium up to the content of 43% calcium; (6) primary grains of  $\text{CaAl}_3$  in the eutectic up to 75% calcium; (7) primary grains of calcium plus the eutectic of calcium and  $\text{CaAl}_3$  up to pure calcium.

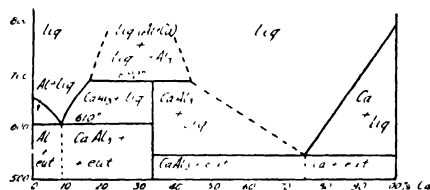
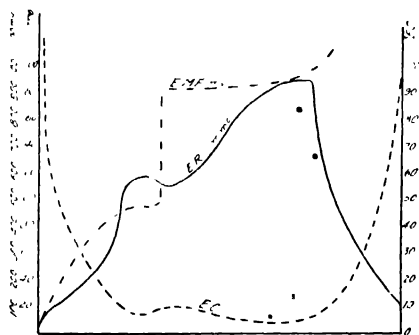


FIG. 16. Const-I diagram by L. Donski (Z Anorg Ch., 1908, v. 57, p. 203)



•The Al-Ca system.

• FIG. 17. Electric properties by Breckenridge. (Am. El. Ch.-I. Soc., 1910.)

As mentioned before, the work of Donsky may be considered as only a preliminary investigation and the aluminum end of the diagram is particularly in need of more detailed

study. Breckenridge (Trans. Am. Elec. Chem. Soc., 1910) investigated the properties of this system as to the way in which its electric conductivity and its electrochemical potential change; his data show that there must be a great deal of solid solubility at the aluminum end of the diagram (Fig. 17). Donsky never proved, even by a microscopical examination, that the eutectic actually appears at a fraction of 1% of Ca as his diagram tends to indicate.

The mechanical properties of aluminum-calcium alloys were never investigated to any extent, although there are a few patents in which an addition of calcium is mentioned either alone and up to 8% for casting work, or in connection with other additions, and up to 0.6% for rolling work. Both cases are represented by quite recent patents.

The chemical properties of aluminum-calcium also were never investigated. It appears, however, according to Breckenridge's diagram (electromotive forces) that the presence of much calcium should make the alloys much more susceptible to corrosion.

It was found quite recently that calcium is able to modify the structure of aluminum-silicon alloys in the same way as sodium if introduced in the melts in amounts up to .1%. This introduction is the more convenient because aluminum forms an alloy with calcium while sodium remains in the form of an emulsion. An auxiliary alloy may be used instead of pure calcium and its distribution through the melt is apt to be much more uniform. Also a slight excess of calcium can hardly affect the alloy in a harmful way.

#### THE ALUMINUM-CERIUM SERIES (Al-Ce)

The thermic constitutional diagram of this system was studied by R. Vogel (Z. Anorg. Ch., v. 75, p. 41). He found the following phases, fields and structures in the complete system (Fig. 18):

<i>Phase</i>	<i>Field</i>	<i>Structure</i>
Pure Al.		
CeAl <sub>4</sub>	Al + CeAl <sub>4</sub>	eutectical
CeAl <sub>2</sub>	CeAl <sub>4</sub> + CeAl <sub>2</sub>	peritectical
CeAl	CeAl <sub>2</sub> + CeAl	peritectical
Ce <sub>2</sub> Al	CeAl + Ce <sub>2</sub> Al	peritectical
Ce <sub>3</sub> Al	Ce <sub>2</sub> Al + Ce <sub>3</sub> Al	eutectical
	Ce <sub>3</sub> Al + Ce	eutectical

Every phase represents here a completely defined chemical substance, but only two of them, namely the CeAl<sub>2</sub> at 1435° and Ce<sub>3</sub>Al at 612°, have definite melting points. The three others form peritectically, when the melt, on cooling, reacts with the previously crystallized phase.

The aluminum corner of the aluminum-cerium diagram was not investigated by Vogel in an exhaustive way. The eutectic between Al and CeAl<sub>4</sub> is located at 638° and 8% cerium. The eutectic temperatures and structures were not positively identified near the aluminum end and it is quite possible that a certain solid solubility exists. Experiments by Barth (Metallurgie, V. 9, p. 261) seemed to indicate that the addition of cerium in aluminum does not result exclusively in the mere presence of the CeAl<sub>4</sub> compound in the eutectic form. A variation of the aluminum corner of the diagram according to Barth is given at the right side of the regular diagram. This experimenter, however, was not sufficiently careful in his work to give reliable information.

At any rate, the action of cerium upon aluminum was never thoroughly investigated. In particular, we do not know how the alloys might be affected by heat-treatment. According to Gillett, who subjected the action of slight additions of cerium to aluminum to an incomplete investigation, the attainable improvements would never pay the costs of the cerium metal introduced in the alloy; still our actual knowledge does not go beyond the most reasonable fact, that 0.2–0.6% Ce will

not produce any substantial change in the structure and properties of either pure aluminum or of Al-Cu alloys in their cast form.

The electrical, physical and electro-chemical properties of the aluminum-cerium system also were never investigated and

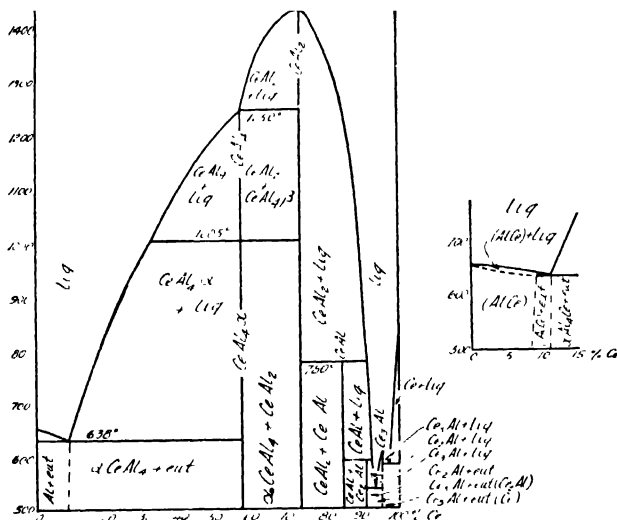


FIG 18. Const-l diagram for the Al-Ce system by R. Vogel.  
(Z. Anorg. Ch., 1912, v. 75, p. 41)

Al-Ce Diagram according to Barth's ideas  
(Metallurgie, v. 9, p. 261.)

so neither they nor the mechanical properties can be represented in the form of diagrams.

The addition of cerium is not mentioned in any U. S. patent dealing with aluminum and its alloys.

### THE ALUMINUM-COBALT SERIES (Al-Co)

This was studied by Gwyer, who developed the constitutional diagram of the aluminum-cobalt alloys in 1908 (Z. an. Ch., vol. p. 113). In this series (Fig. 19) he found a number of definite compounds of which the one having the formula CoAl melts at 1628° and is able to retain, in the form of a

solid solution, quite a large quantity of cobalt in such a way as to form a monophasic field from about 68% to 86% cobalt at high temperatures. This field seems to narrow down by a precipitation of the metallic cobalt phase at temperatures below 800°. Metallic cobalt may also retain up to 9% aluminum in the form of a solid solution at higher temperatures, and possibly a slightly smaller amount at temperatures below 800° when the beta cobalt changes presumably to alpha. Alloys of cobalt with aluminum belonging to this field of solid solutions at the cobalt end of the diagram were never investigated as to their mechanical properties and possible applications. We venture to say that they might be quite useful in the field of thermocouples manufacture.

Between 0 and 68% cobalt we find two more compounds; one believed to be  $\text{Co}_2\text{Al}_7$  and another,  $\text{CoAl}_4$ . Both form peritectically by reaction between the primary compound higher in cobalt and the remaining liquid. The compositions of these compounds cannot be considered as definitely known.

At the aluminum end of the diagram we become impressed with the fact that eutectic is shown as located rather near to pure aluminum and possibly not containing over 0.5% cobalt in the eutectic state. An increase in the amount of cobalt results therefore in a very quick rise in melting temperature, which fact makes the production of aluminum-cobalt alloys of higher cobalt contents quite difficult.

Notwithstanding this fact, Schirmeister in 1911 (*Metalurgie*, Vol. 8, p. 650) was able to make alloys containing up to 14% cobalt and he found that, while his cast ingots showed a decrease in strength with the first additions of cobalt, the properties were decidedly improved within the field from 9 to 13% cobalt, the castings having also a much better appearance. He was also able to hot-roll his ingots up to 7% cobalt and tested them in the annealed (2 hours at 350°) state. His results are shown in Fig. 20. It seems that up to 4% cobalt the strengthening of the alloy proceeds in a very continuous manner, suggesting that the real eutectic is located at this composition. Above 4% cobalt, the hardness remains almost



constant at 48 to 50 Brinell, while the ultimate strength increases steeply once more, retarding again at 6% cobalt. The ductility is decreased continuously up to 4% cobalt, at which composition the small-gage sheets show an elongation of 19%

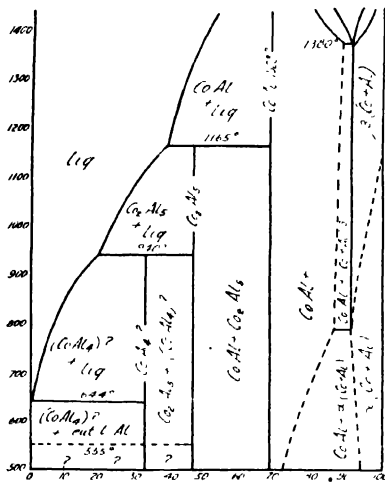


FIG 10 Const-l diagram of the Al-Co series by Gwyer  
(Z. An Ch, 1908, v. 57, p. 113)

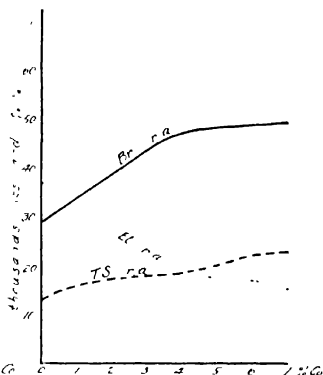


FIG 20 Mech properties of Al-Co alloys as rolled and annealed

in 2 inches. Accordingly, as much as 4% cobalt may represent a desirable addition for the rolled metal. Yet the actual effect per unit of added metal is not so great with cobalt as it is either with copper at higher percentages, or with chromium at low percentages. While the use of cobalt in castings does not look promising, we have to mention the statements by Schirmeister and also by Neuburger, who believe that about 10% cobalt might produce useful casting metal.

Only one U. S. patent, which expired long ago, mentions cobalt as a desirable addition to aluminum, without giving the actual cobalt content.

## THE ALUMINUM-CHROMIUM SERIES (Al-Cr)

Aluminum-chromium alloys were roughly investigated by L. Hindrichs (Z. An. Ch., 1908, vol. 59, page 430) and his meager data were developed into a diagram by Professor Guertler. Some contradictions in the latter's comments compelled the author to introduce a few extra changes which resulted in the diagram of Fig. 21.

It seems that the actual solubility of chromium in molten aluminum is rather low; up to  $980^{\circ}$  only 2% chromium may

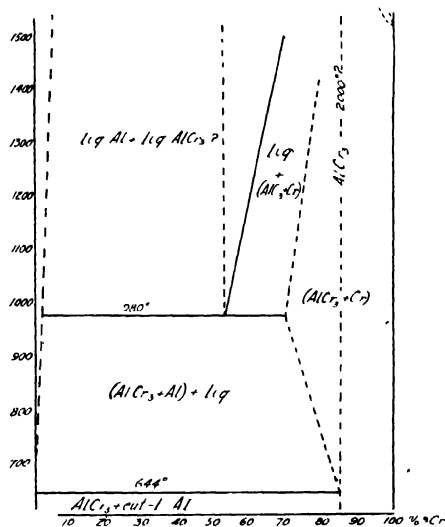


FIG. 21. Const-l diagram of Al-Cr series, data by L. Hindrichs.

(Z. An. Ch., 1908, v 59, p. 430.)

Developed by Guertler and changed by the author.

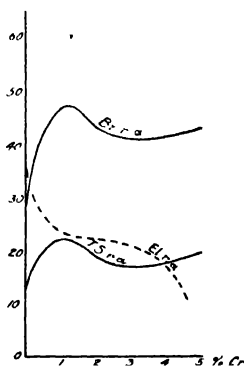


FIG. 22. Mechanical properties of rolled and annealed Al-Cr alloys.

be introduced in the alloy so as to become completely dissolved. All chromium introduced into aluminum forms a compound  $\text{AlCr}_3$  which should, according to the diagram, crystallize first, practically under any condition and however small the content of chromium.

The compound mentioned seems to form and to freeze at  $2000^{\circ}\text{C}$ ., and presumably can retain in the form of a solid solu-

tion, comparatively large amounts of chromium or aluminum. In the liquid state it dissolves aluminum and keeps it in solution until, due to the precipitation of the compound, the remaining liquid attains the temperature of  $980^{\circ}$  and contains about 54% chromium. At this point, according to the diagram, the excess of aluminum separates in the form of an independent layer, while the remaining liquid continues to precipitate the aluminum-chromium compound (highly saturated with aluminum) in the form of a solid solution.

The first conclusion to be drawn from the diagram seems rather unfavorable to aluminum-chromium alloys; it tends to show that to introduce as much as 1% chromium we must raise the temperature of aluminum at least to  $900^{\circ}$  before pouring. Under these conditions the alloy might be burned quite materially and neither good castings nor good ingot metal would be obtainable, which condition would be still further aggravated by the segregation of primary  $\text{AlCr}_3$  crystals due to their higher specific weight.

Actual experience, however, shows that the conditions are much more favorable. Thus Schirmeister used to introduce up to 5% chromium into aluminum without observing any segregation or a separation of the melt into two layers; all his alloys rolled well and in the annealed state every one of them was stronger than pure aluminum (Fig. 22). The fact of particular importance is that with about 1% chromium we have quite a high increase in strength in the annealed state and a still higher increase in hardness, which latter exceeds everything obtainable by the addition of Fe, Ni, Co, Mn or Si at much higher percentages. Elongation, which falls continuously with the addition of chromium, remains fairly good (in the annealed state) at 3.5% chromium and very satisfactory at 1% chromium. The addition of chromium appears still more advantageous if we consider the service of the alloys at high temperatures, where chromium permits the alloy to retain high hardness and high strength to an extent at least comparable with that obtained by the use of much larger quantities of either nickel or cobalt. .

The comparatively great reduction in the melting point of pure aluminum at the addition of mere traces of chromium as shown in the diagram ( $644^{\circ}$  instead of  $658^{\circ}$ ) arouses suspicions that the eutectic composition lies actually at some substantial amount of chromium and not at mere traces. The aluminum end of the diagram awaits therefore a more thorough investigation.

The influence of chromium upon the mechanical properties of aluminum either in the cast or the hard-rolled state has not yet been investigated, and similarly nothing is known about the electrical, thermal and chemical properties of the series.

Chromium is specified in one old U. S. patent as an alloying element for aluminum castings, and more recently it is successfully used as a material component of a variety of duralumin, which use is also covered by a patent.

## THE ALUMINUM-COPPER SERIES

In its practical applications, the aluminum-copper series is by far the most important of all aluminum alloys.

The constitutional diagram for aluminum-copper alloys was first studied intensively by Carpenter and Edwards (8th report to the Alloys Research Committee — Institution of Mechanical Engineers, 1907). Afterwards it was reinvestigated by numerous experimenters, among them being Curry (Jour. Phys. Chem., vol. 11, p. 425, 1907) and Gwyer (Z. An. Ch., vol. 57, p. 103). The most recent investigation, and the most elaborated from the viewpoint of the constitutional diagram, is that of D. Stockdale (Jour. Inst. Met., 1924, Vol. 31, p. 275), whose diagram is represented in our Fig. 23. Two definite compounds  $\text{Al}_2\text{Cu}$  and  $\text{AlCu}_3$  are known in this system. The second is the basis of the beta phase of aluminum bronzes and has a maximum melting point at  $1050^{\circ}$ . The first forms only peritectically at  $585^{\circ}$ . Within the interval from 54 to 87% aluminum other compounds are formed, which retain different

amounts of aluminum and copper in solid solutions but are not very stable and undergo different changes. Two such compounds, probably  $\text{Al}_2\text{Cu}_1$  and  $\text{Al}_2\text{Cu}_3$ , might form the basis of the phases  $\delta$  and  $\epsilon$  as shown in the diagram.

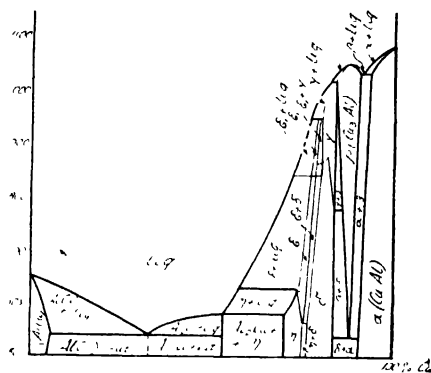


FIG. 23. Const-1 diagram of Al-Cu series by D. Stockdale (J. I. M., 1924 (XXXI), p. 275)

At the aluminum end of the diagram we find copper lowering the melting point of aluminum quite substantially until the eutectic at 34% copper and at a temperature of  $540^\circ$  is reached. This eutectic is composed of the compound  $\text{Al}_2\text{Cu}$  and a solid solution of copper in aluminum. The first investigators of this system did not ascertain the solubility limit of copper in solid aluminum and its change with temperature. Therefore they assumed the solid solubility to stop at 3% copper and to remain practically constant. Later investigations have shown this not to be the fact and now the solid solubility at the eutectic point is believed to be about 5 to 7% copper. The decrease of the solid solubility with temperature, *i.e.*, the actual location of the solid solubility line, is not yet known. We are quite certain that in the state of equilibrium at  $200^\circ\text{C}$ . no more than 2.0% copper may remain in the solid solution and that this limit is not further reduced when the temperature becomes normal.

The variable limit of solid solubility of copper in aluminum and the decrease of this solubility with temperature make it

possible to modify aluminum-copper alloys by heating them to  $500^{\circ}$  to  $525^{\circ}$  C. and quenching. In this case theoretically as much as up to 6 to 7% Cu should be preserved in a solid solution state with its peculiar properties — high electric resistance, higher ductility, a slightly increased hardness, etc.

Quenching followed by either ageing or a suitable tempering at some elevated temperature, but much below the solubility line, should produce a state of increased hardness and strength with good ductility, by precipitating the excess copper in the form of finely distributed ultra-microscopic  $\text{CuAl}_2$ .

Experimental investigations actually corroborate these theoretical conceptions about the effect of quenching and hardening in alloys from 2.5 to 5.0% copper at least, as shown in Fig. 24. Still better and much more constant results are

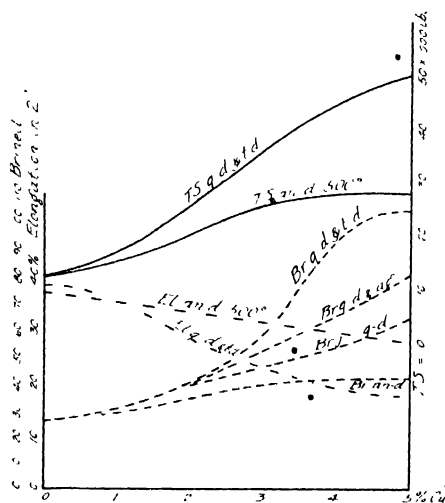


FIG 24. Effects of heat treatment upon the properties of Al-Cu alloys in the rolled state.

(J. I. M., 1923 (XXIX), p. 492.) Hanson & Gayler.

obtainable, however, by the heat treatment of the complex duraluminum alloys discovered and introduced into general use long before experiments with the plain aluminum-copper alloys were undertaken.

Some physical properties of the aluminum-copper system were studied by Broniewski (C. R., vol. 149, p. 853). He studied the electric conductivity of the alloys as cast and afterwards either annealed or chilled. The graphs he obtained are represented in Fig. 25. He also studied the electrochemical

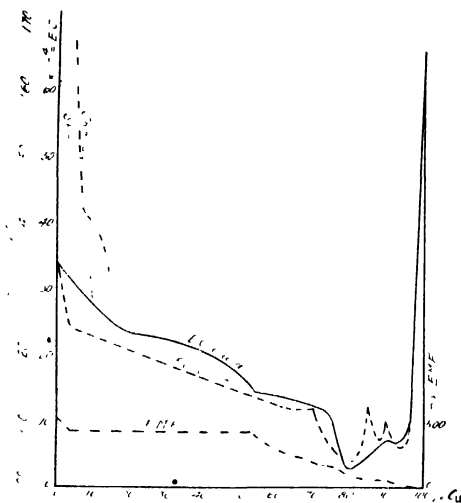


FIG. 25. Electric properties and shrinkage of Al-Cu series

potentials and found that up to 4% copper (in the annealed state) the potential of the alloys becomes more noble and stays so up to the composition at which the  $\text{Al}_2\text{Cu}$  compound forms a pure phase. From this point the electrochemical potential recedes in a very complicated way until it reaches the potential of pure copper. Broniewski's findings interest us inasmuch as they show that the addition of copper must help aluminum to form less corrodible alloys. On the other hand, we see that the electrochemical potential of aluminum bronzes is higher than that of copper, while we know their corrodibility to be lower. The last fact is good evidence that the electrochemical potential cannot be fully relied upon in the study of the chemical properties of alloys.

The influence of copper on the mechanical properties of

aluminum is quite substantial (Figs. 26, 27). The ultimate strength of cast metal is increased continuously and almost in direct proportion. With the chill-cast alloys the rate of increase in strength is higher at lower percentages, becomes slightly less at about 5%, and then rises again. Elongation is

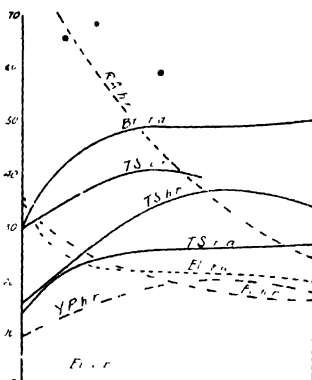


FIG. 26 Mechanical properties of Al-Cu alloys as worked

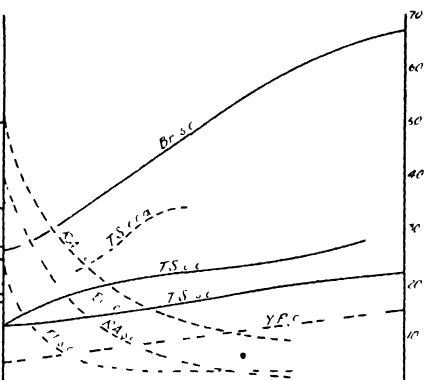


FIG. 27. Mechanical properties of Al-Cu alloys as cast.

affected quite strongly in the sand-cast and much less so in the chill-cast state. Yet the mechanical properties of both sand-cast and chill-cast aluminum-copper alloys are so uniform, if cast under constant and carefully controlled conditions, that they form the largest bulk of aluminum-base castings used in the United States. The composition of cast aluminum-copper alloys does not exceed 14% copper.

Diagram Fig. 25 shows also the extent to which shrinkage of aluminum is affected by additions of copper in both sand-cast and the chill-cast state. The lowest amount of shrinkage is reached at about 14% copper, when it is 1.19% for chill castings and 1.33% for sand castings. In spite of the fact that these figures for shrinkage were obtained by very reliable investigators, they cannot be considered as representing the actual situation in foundry practice, inasmuch as the problem of shrinkage is very difficult of solution.

Alloys of aluminum with copper are also widely used in the



rolled state. It takes only 3.5% copper or about the limit of maximum solid solubility (under a regular rolling mill practice) to raise the strength of cold-rolled metal to 40,000 pounds per square inch. In the annealed state the best conditions are obtained at approximately 4% copper, when, the strength is 26,000 pounds, the ductility 22%, and the Brinell hardness 49. With hot-rolled metal the best properties are reached at about 5.5% copper, where 37,000 pounds per square inch, 18% elongation, and 37% area reduction can regularly be obtained. Accordingly, these alloys containing 3.5 to 5.5% copper are the most frequently used in rolling-mill practice to obtain hard, strong metal, useful for the same purposes as soft aluminum, and having a good chemical stability against tap water and such liquids as are used in the household and in some industries.

### THE ALUMINUM IRON SERIES (Al-Fe)

The aluminum-iron system was first investigated by Gwyer (*Z. an. Ch.*, 1908, p. 126-133), the results of whose investigation are produced in Fig. 28 in a form developed by Guertler and to a certain extent modified by the author. According to this diagram, the introduction of the merest trace of iron increases the melting point of aluminum. The eutectic seems to coincide with pure aluminum, any excess of iron crystallizing primarily and in the form of a compound  $\text{Al}_3\text{Fe}$  which seems to be able to retain a certain extra amount of iron in its lattice. At normal temperatures, according to Guertler, the system shows the following fields and structures:

(1) Phase	Field	Structure
Pure Al		
$\text{Al}_3\text{Fe}$ + excess Fe	$\text{Al} + (\text{Al}_3\text{Fe})$ $(\text{Al}_3\text{Fe} + \text{Fe})$ $(\text{Al}_3\text{Fe} + \text{Fe}) + \text{Al}_2\text{Fe}$	eutectical homogenous peritectical
$\text{Al}_2\text{Fe}$		
(Fe Al)	$(\text{Al}_2\text{Fe} + (\text{Fe Al}))$ $(\text{Fe Al})$	eutectical homogenous

Guertler believes the ferrite (Alpha iron) to be unable to retain much aluminum in solid solution, while the gamma iron might do so up to 35% aluminum at a temperature of about  $1000^{\circ}\text{C}$ .

The same system was investigated by Kurnakov in 1919. In the diagram which he developed (Fig. 30) we have the phases  $\text{FeAl}_2$  and  $\text{Fe}_2\text{Al}_3$ . He finds the solid solubility of

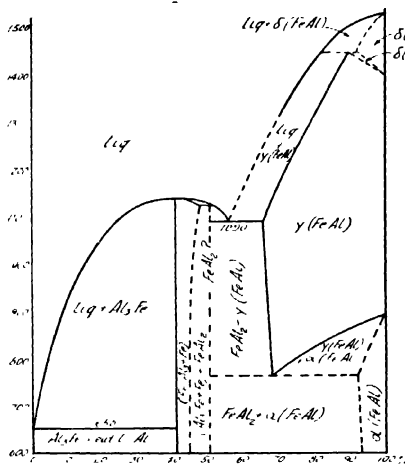


FIG. 28 Const-l diagram of the Al-Fe system by Gwyer, developed by Guertler and slightly changed by the author.

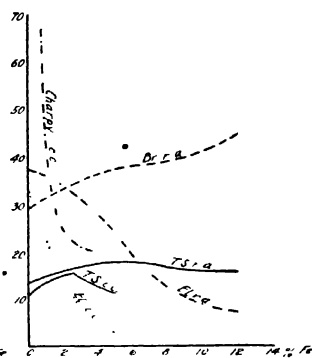


FIG. 29 Mech. properties of Al-Fe Alloys.

aluminum in both alpha and gamma iron to be almost the same and to be limited (in the cast and annealed state) by the 65% Fe. composition.

Neither Gwyer nor Kurnakov investigated a sufficient number of alloys at the aluminum end of the diagram to be able to state positively that aluminum crystallizes secondarily at the merest traces of iron. In view of the fact that the primary of the crystallization of either aluminum or  $\text{Al}_3\text{Fe}$  may have an important bearing upon the manner in which iron influences the properties of aluminum, the actual conditions at the aluminum end must be considered as open to discus-

sion. However, it is known beyond doubt that aluminum actually does not retain in solid solution more than mere traces of iron, and accordingly iron cannot be expected to noticeably affect such properties as are connected with the form and structure of the crystalline lattice.

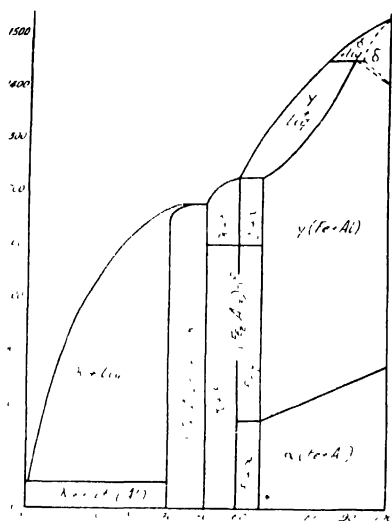


FIG. 30 Const-l diagram of the Al-Fe series by Kurnakov.

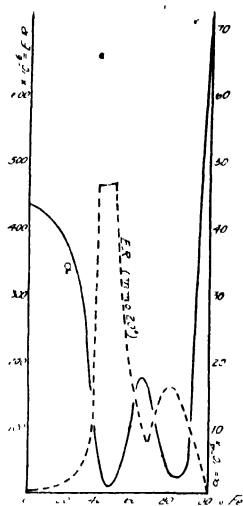


FIG. 31 Electric properties of Al-Fe series by Kurnakov.

The electric properties of aluminum-iron alloys were also investigated by Kurnakov, whose graphs are given in Fig. 31. As Kurnakov omitted to investigate any alloys below 35% iron by weight, the actual influence of small additions of iron upon the electric properties of aluminum may not be represented with enough precision.

Other physical and chemical properties of this system have not yet been investigated. We find, however, a lone statement to the effect, that with an increase in the amount of the needle-like crystals of  $\text{FeAl}_3$  the alloys become more stable atmospherically.

The influence of iron upon the mechanical properties of chill-cast aluminum is shown in Fig. 29, drawn from the ex-

periments of the British Light Alloys Sub-Committee published in 1921. The slight gain in strength imparted by iron up to 2.5% is decidedly offset by the pronounced decrease in ductility. The maximum increase of strength occurring at 2.5% Fe indicates that the eutectic composition does not lie probably below 2% Fe.

A great deal of distrust attaches to the presence of iron in aluminum alloys either for casting or for working purposes. It seems, however, that this distrust (if it is reasonable at all) must have arisen from the peculiar influence of iron upon the appearance and soundness of the cast metal rather than from any effect upon mechanical properties. At any rate, iron helps aluminum to retain its hardness and strength at comparatively high temperatures.

The influence of iron upon the mechanical properties of hard-worked aluminum has not yet been studied; its influence upon rolled and annealed alloy sheet is also shown in Fig. 29. We see that iron substantially and continuously increases the hardness but rather unfavorably affects the elongation. However, at about 6% iron the elongation is still quite fair, the hardness sufficiently high, and the strength improved by at least 30%.

In spite of the fact that iron is regarded with great suspicion as an alloying element for aluminum, it is mentioned as a secondary element in five U. S. patents, particularly as an additional element in alloys containing copper, zinc or both.

#### ALUMINUM-GERMANIUM, ALUMINUM-INDIUM, ALUMINUM-THALLIUM SERIES (Al-Ge, In, Tl)

The mentioned metals, although rare, are coming more and more within the reach of the industries. Germanium was quickly found to be a valuable alloying element for copper, with which it produces very hard and strong solid solutions. It is quite probable that alloys of aluminum with small amounts of germanium will prove to have some industrial value. On

the other hand, indium and thallium do not look promising, as they should behave with aluminum in much the same way as lead. Nothing is yet known about the real relations in this field, as no experimental study has been undertaken.

#### THE SERIES ALUMINUM-SODIUM AND ALUMINUM-POTASSIUM (Al-Na and Al-K)

Both sodium and potassium have very low melting points and high atomic volumes; furthermore they crystallize in the body-centered cubic system whereas aluminum crystallizes as a face-centered metal. Accordingly, the impossibility of alloying aluminum with either sodium or potassium might have been foreseen and it was actually found that both metals form separate layers at any temperature up to their boiling points. This property was even made use of recently in a process for refining aluminum-silicon alloys. A slight amount of sodium, say 0.1%, introduced into an Al-Si alloy does not actually alloy with it but forms a substantial amount by volume which, in some still unknown way, suffices to introduce variations in the shape and size of the eutectic grains of silicon, making them less sharp, less hard, much smaller, and more intimately connected to the grains of aluminum. The refusal of aluminum to alloy with either sodium or potassium compels any remaining excess of the alkaline metal to leave the molten mass and therefore no undesirable mechanical or chemical influence imparted by the alkaline metal is encountered in the Al-Si alloys so treated.

On the other hand, an opinion still exists in metallurgical circles that slight amounts of sodium may remain in aluminum, whether as a natural impurity unavoidable in the electrolytic manufacturing process, or as an artificial addition. This excess sodium is thought to be very undesirable in its effect upon the mechanical reliability and particularly the chemical stability of the metal. The latest experiments of Czochralski uphold the opposite idea, that sodium has almost

no chance to remain in aluminum, and particularly that even substantial amounts of sodium introduced into aluminum before casting have no noticeable influence upon the properties of the wrought aluminum products.

### THE ALUMINUM-LITHIUM SERIES (Al-Li)

Lithium, while alkaline, is also largely analogous to magnesium. Minerals containing it are quite numerous and it may be manufactured at a comparatively low cost in the electrolytic way. There is also a strong possibility that fused salts containing both lithium and aluminum might produce alloys of these metals by electrolytic reduction, and it is equally possible that aluminum itself will be able to reduce certain molten lithium salts quite efficiently.

The low atomic weight of lithium (less than one-third that of magnesium) might make it possible to achieve the special hardening effects with a much smaller amount of lithium than can be obtained with magnesium. In fact, lithium easily forms a silicide of the elementary composition  $\text{Li}_3\text{Si}$ , where 21 parts of lithium by weight are equivalent to 48 parts of magnesium. This compound,  $\text{Li}_3\text{Si}$ , might take the place of  $\text{Mg}_2\text{Si}$  in producing the ageing effect. The boiling point of lithium is high enough to prevent it from escaping from liquid aluminum and the alloying process would probably not be difficult.<sup>1</sup>

### THE ALUMINUM-MAGNESIUM SERIES (Al-Mg)

This has been the subject of a great deal of investigation. For a long time the system was considered as embracing two

<sup>1</sup> There was a rumor heard for the last year, that lithium was found by German metallurgists to have a particularly strong hardening effect upon aluminum. The most reliable information is however that an aluminum alloy containing numerous additions and called "Scleron" actually contains lithium also. The mechanical properties of this "Scleron" alloy are in no way spectacular and fall much below those of any duralumin composition.

For newest data on the Al-Li system see appendix.

structural fields; in one, the eutectic was considered as being formed by aluminum and the compound  $\text{Al}_4\text{Mg}_3$ , either of which might crystallize primarily; in the other, the eutectic consisted of the same compound and pure magnesium. No solid solutions were observed by the early authors. Within the last five years the influence of magnesium upon aluminum alloys has become a very important subject of investigation, and a complete diagram was elaborated by Hanson and Gayler; it shows the presence of two homogeneous fields of solid solutions based upon the compounds  $\text{Al}_7\text{Mg}_2$  and  $\text{Mg}_3\text{Al}_2$  in the central part of the system. The English investigators found also that at the aluminum end the solid solutions go up

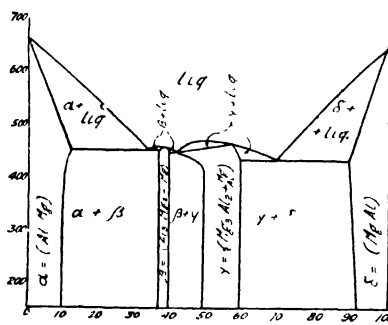


FIG. 32 Const l diagram of the Al-Mg series by Hanson & Gayler (J. I. M., 1920, v. 2, p. 201)

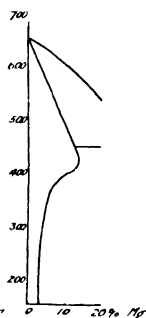


FIG. 33 Const l diagram of Al-Mg series by Sander & Meissner (Z. Metallkunde, 1923)

to 10% magnesium and that saturation remains practically constant at any temperature almost up to incipient fusion. German investigators (Sander and Meissner) found the data of Hanson and Gayler to be essentially correct; they believe, however, that the limit of solid solubility of magnesium in aluminum does not hold at 10% for every temperature, but decreases quite rapidly from about 12% at 425° to 5% at 350°, and then recedes much more slowly until normal temperature is reached (Figs. 32-33). According to the English investigators it is impossible to obtain aluminum-magnesium

alloys in a supersaturated state by quenching due to the constancy of the saturation limit. According to the Germans this state can be achieved by heat-treating the alloys in the range of  $410^{\circ}$  to  $425^{\circ}$ , and quenching. The precipitation of magnesium in the form of  $\text{Al}_3\text{Mg}_2$  proceeds so rapidly, however, that only a small part of the complete saturation at high temperatures can be preserved at normal temperature. Furthermore, the necessary heat-treating range is dangerously near the temperature of incipient fusion, whence the handling of the alloy becomes very difficult.

Aluminum-magnesium alloys have been quite prominent, and a number of advantageous features were claimed for them, besides the obvious fact that such alloys must actually be lighter even than pure aluminum. We have heard of rolling alloys containing up to 5% magnesium, regular casting alloys containing about 10% (and over), and special casting alloys with 30% magnesium believed to be highly sonorous and to take a mirror-like polish.<sup>1</sup> These various alloys were known under the collective name of magnalium and, strange as it may appear now, as much as 62,000 pounds per square inch was claimed for casting alloys with 10% magnesium.

According to Mach, a strength of 18,000 lbs. is obtainable in a 2% Mg alloy (sand casting), while 21,500 lbs. and a 2.5% elongation in 4" are the figures for 10% Mg. The mechanical properties of either cast or rolled Al-Mg alloys undoubtedly follow a queer law, but figuring from the strength of the annealed rolled alloys we may safely expect at least 32,000 lbs. 10% and 25,000 lbs. at 5% of magnesium under properly adapted casting practice.

It is doubtful whether any alloys containing even so much as 5% magnesium are now being used in quantities. Magnesium is quite an expensive metal, and is apt to burn and to form nitrides, thus contaminating the alloys. Furthermore, it is entirely unreasonable to expect an increase in chemical resistance through the influence of magnesium. Such alloys as contain free  $\text{Al}_3\text{Mg}_2$  are quickly attacked by the purest water. In melting practice magnesium produces a large amount of



dross. The whole operation of making aluminum-magnesium alloys in the finished form seems to be very fussy and tedious and it is clear why these alloys are now practically discarded. Nevertheless, it is quite remarkable that this system was never systematically investigated as to its mechanical properties, in view of the high claims made for the magnalium alloys.

We know practically nothing about the actual effects of magnesium upon the mechanical properties of cast aluminum. In 1910, H. M. Lane proposed to use magnesium as a deoxidizer for aluminum and made quite a number of experiments for the purpose of investigating the influence of magnesium upon aluminum when repeatedly remelted and recast. He went up to 3.5% magnesium but was unable to achieve any uniformity of results, while quite naturally so large an amount as 3.5% of an additional metal cannot be supposed to act only as a deoxidizer. It may be said that with good foundry practice an addition of 3.5 magnesium will raise the ultimate strength of cast aluminum up to 19,000 and possibly to 22,000 pounds, while the elongation will drop almost to 3%. These figures taken alone indicate that it may be possible to obtain fairly strong castings with the use of a comparatively small amount of magnesium and to gain a substantial saving in weight. A well-established and valuable feature of magnesium is the pronounced reduction of shrinkage it causes in cast aluminum. This reduction amounts to 0.06% per 1% Mg in chill castings and to 0.05% in sand castings. The lack of a systematic investigation into the properties of cast aluminum-magnesium alloys, and particularly their chemical resistance, makes it impossible to pass a final judgment.

A superficial investigation by the author showed at least that the hardness of aluminum is increased enormously by alloying with magnesium, and that the amount of hardening produced increases continuously with the further addition of magnesium up to at least 27% of the latter. The hardening effect per unit weight of magnesium seems to be larger than that produced by the unit weight of any other common metal. (Fig. 34a.)

The luster of the alloy becomes more brilliant with the increasing addition of magnesium, and at 20% of the latter the chill-cast metal has a pronounced silvery appearance. The corresponding effect is not so marked in the metal which was furnace-cooled and had a chance to acquire a rough-grained texture.<sup>1</sup>

Old authorities mention also that the aluminum-magnesium series shows an increase in chemical sensitivity up to 3% Mg, then a decrease between 3% and 10%, and a new increase above this limit.

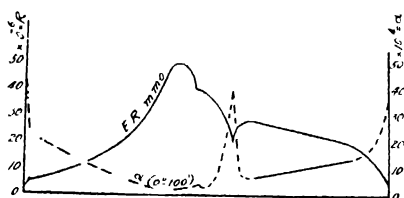


FIG. 34. Electrical properties of the Al-Mg series by Broniewski

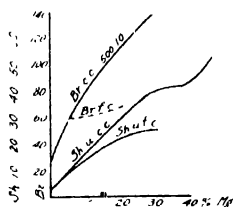


FIG. 34a. Hardness of Al-Mg alloys by Korsunsky

The first and second parts of this statement require corroboration. In the chill-cast alloys with 20% and 30% Mg, the stability of the silvery luster seems to show at least that the high resistance to atmospheric corrosion in the region rich in  $\text{Al}_3\text{Mg}_2$  is an actual fact.

Alloys with approximately 5% Mg are decidedly tough and their fractures silky with a dull luster. At 10% Mg they are not yet excessively brittle. The impact resistance is, however, very small and the fractures earthy white. Somewhere below 20% Mg the actual brittleness begins and at least up to 45% Mg the mechanical properties are bad. The fractures become, however, lustrous and microcrystalline somewhere below 30% Mg.

<sup>1</sup> The mirror-like surface of polished aluminum-magnesium alloys containing 30% Mg was first mentioned by Hagen and Rubens in 1902, in connection with the reflecting properties of these alloys in the ultraviolet. More recently Waltenberg and Coblenz, of the U. S. Bureau of Standards, reinvestigated the 30% Mg composition and found that the latter reflects light, and particularly the ultraviolet rays, actually much better than silver or stellite. They found, however, that the reflecting surfaces obtained in aluminum-magnesium do not resist atmospheric corrosion for a sufficiently long time. (Sci. Pap. No. 363.)

According to the data by Schirmeister, the presence of magnesium in aluminum in the rolled and annealed state has an important influence upon strength, hardness and ductility. His rolling experiments showed that it is not altogether easy to roll high-magnesium alloys, at least under the regular rolling mill practice. Still it is quite possible to obtain a strength of 35,000 lbs. in a 5% Mg alloy, with an elongation of 22% and a hardness of about 60 Brinell.<sup>1</sup> These features, as represented in Fig. 35, show that an offhand discarding of aluminum-magnesium alloys is not warranted, and that while they may not be entirely successful under usual foundry conditions, a scientific investigation may throw light upon methods of work capable of yielding valuable alloys in this system.

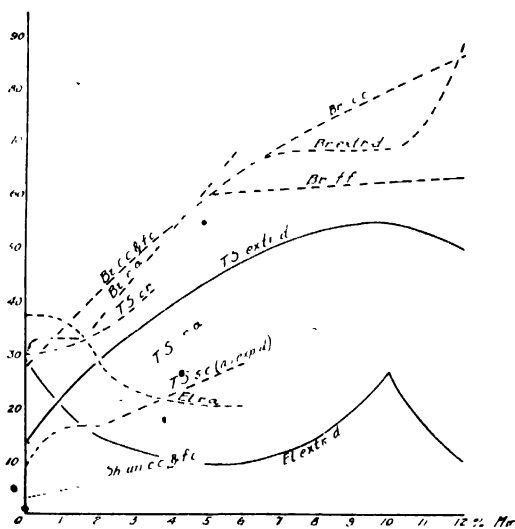


FIG. 35 Mechanical properties of Al-Mg alloys

The electrical properties of aluminum-magnesium alloys are shown in Fig. 34, as drawn by Broniewski in 1911 (C. R. 152, p. 87). They indicate that up to 2% magnesium a solid

<sup>1</sup> More recently (Zeit. fur Metallkunde, 1924, p. 60) Wetzel described the mechanical properties of aluminum-magnesium alloys in the form of extruded rods 8 mm thick. His data go up to 12% Mg; a slightly idealized representation of the corresponding features (ultimate strength, Brinell hardness and elongation) is given in Fig. 35.

solubility exists in the annealed alloy, also that at about 57% magnesium a phase exists with quite a high conductivity and possibly also a high ductility. The e.m.f. curve shows that an addition of magnesium makes the potential less noble and a substantial decrease in chemical resistivity might be expected unless counteracted by some additional features. This latter graph was developed by Broniewski, who did not take the precaution to use alcoholic solutions for the potential determination, as specified by Breckenridge in 1908 during his work on the aluminum-calcium series. The potentials of the aluminum-magnesium system in aqueous solutions are so heavily burdened with electro-motive forces from side-reactions that no safe conclusions can be drawn from Broniewski's data.

Magnesium is mentioned as an important addition to aluminum for casting work in twelve, and for rolling work, in ten U. S. patents.

#### THE ALUMINUM-MANGANESE SERIES (Al-Mn)

The aluminum-manganese system was first investigated by L. Guillet. His work, however, was far from precise and the system had to be reinvestigated by Hindrichs, who succeeded in throwing much more light upon the constitutional diagram, although the latter can even yet hardly be considered as more than approximately known. The most interesting points of the diagram by Hindrichs (Fig. 36) seem to consist in the presence of two ranges of compositions in which the liquid state is represented by one liquid compound and the liquid excess of some other melt, forming two separate liquid layers. This separation does not, however, become an actual fact under practical conditions, the alloys forming emulsions or suspensions more or less uniform in structure. At the normal temperature we find the following phases and fields:

Phase	Field	Structure
Aluminum		
M Al <sub>3</sub>	Al + MnAl <sub>3</sub>	eutectical
MnAl	MnAl + MnAl <sub>3</sub>	eutectical
Mn <sub>3</sub> Al	MnAl + Mn <sub>3</sub> Al	peritectical
Manganese	Mn <sub>3</sub> Al + Mn	eutectical

We are also interested in the fact that the eutectical point between aluminum and the compound richest in aluminum is situated at about 3% manganese, which means that up to

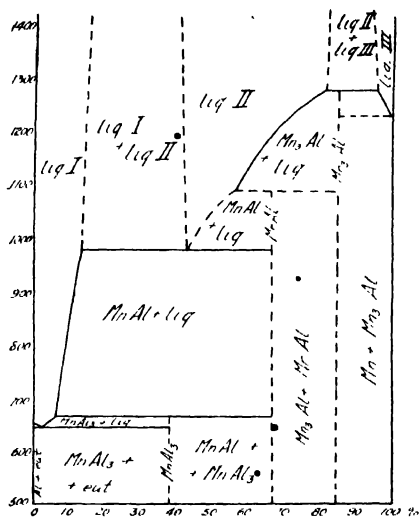


FIG. 36. Const-l diagram of Al-Mn series according to Hindrichs

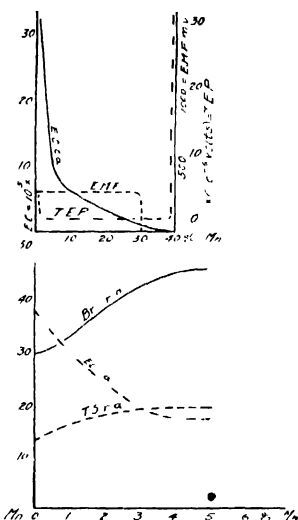


FIG. 37. Mech prop of rolled and annealed Al-Mn alloys.

FIG. 38 (above). Electric properties of Al-Mn alloys.

this point the addition of manganese must be quite easy, and that MnAl<sub>3</sub> crystallizes eutectically, increasing the strength of the alloy without seriously impairing its ductility. Manganese can be introduced quite easily even up to 6%, the first difficulties being encountered at say 10% manganese, which is, however, much beyond the limits of alloys used in practice.

No systematic investigation was ever undertaken to show the influence of manganese upon the mechanical properties of aluminum either as cast or in the hard-worked state. According to Schirmeister (Fig. 37) an addition of manganese up to 5% favorably influences the strength and hardness of the annealed sheet metal and while it reduces ductility this does not reach the danger point. He found the rolling properties of these alloys to be rather good in both the hot and the cold state.

The electric properties of aluminum-manganese alloys

### ERRATA

Page 61, 2nd paragraph, last line should read "running up 1 or Manganese "

Manganese is listed as an alloying element in three U. S. patents dealing with casting alloys, and in two relating to wrought alloys; the specified amounts never exceed 3%. It is used with particular frequency as an alloying element in making duralumin and similar alloys in which it increases the strength at the higher temperatures and also affects favorably the chemical resistance. Nickel and particularly chromium are well suited to replace manganese in this direction.

An alloy of aluminum with 1.25-1.50% Mn is widely used in America in the wrought form under the trade mark of 3S. It is most adapted for strong, reliable and inexpensive articles produced by spinning, stamping, etc., and requiring no heat treatment. Alloys with 2-3% Mn were developed by the U. S. Navy for casting purposes and seem to become popular.

### ALLOYS OF ALUMINUM WITH MOLYBDENUM, TANTALUM, THORIUM, TUNGSTEN AND URANIUM

Alloys of aluminum with the five mentioned high-melting and strongly metallic elements have not yet been sufficiently investigated. Schirmeister experimented on alloys of alumi-

num, with molybdenum, tungsten and tantalum, averaging about 5% of the additional metal. He found that no one of them was able to affect aluminum advantageously, but all of the alloys rolled sufficiently well. The best results were obtained with molybdenum, which increased the ultimate strength in the rolled and annealed state by approximately 22% at an addition of 0.7% molybdenum; the hardness of the metal was increased slightly, while the ductility remained practically the same. Aluminum-uranium alloys have not yet been examined. We may say of all these metals in general that the slight improvement in strength that they impart to aluminum can be attained more cheaply with more common metals.

Schirmeister found also that aluminum treated with one of these high-melting metals possesses a much better macrostructure, *i.e.*, the grains in the fracture are more refined and directional crystallization in the chill-cast ingot is less apparent. However, his observations were not numerous enough to permit a positive conclusion as to the refining action of these metals upon chill- or sand-cast aluminum and its alloys.

The same author found that the addition of about 0.5% of either molybdenum or tungsten to alloys of aluminum with cobalt, containing about 10% of the latter, increased substantially the strength in the cast state, refined the grain, and produced a better ductility. These observations also were too few to prove anything conclusively.

The series aluminum-molybdenum was recently investigated by Reiman, who produced the alloys by a reduction process starting from molybdenite. He obtained alloys up to 12% molybdenum and developed a hypothetical constitutional diagram (Fig. 39). He mentions the existence of two definite compounds,  $\text{Al}_3\text{Mo}$  and  $\text{Al}_2\text{Mo}$ , which are formed peritectically in the molten alloys of aluminum with molybdenum, the  $\text{Al}_3\text{Mo}$  being the more stable at low temperatures and small amounts of molybdenum. He found also that neither large nor small contents of molybdenum improve the mechanical or chemical properties of the cast metal.

The aluminum-thorium system was subjected to a pre-

liminary study by L. Guillet. The difficulty of obtaining pure thorium and of producing alloys by the thermit reduction is greatly increased by the enormous stability of thorium oxide.

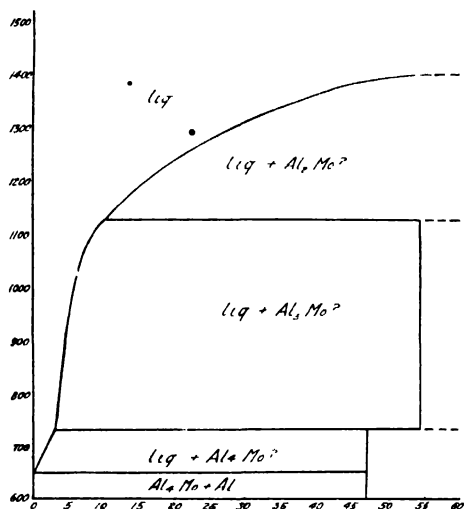


FIG. 30. Hypothetical const-l diagram of the Al-Mo series.

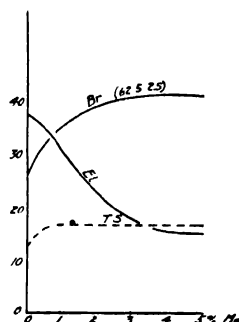


FIG. 40. Mechanical properties of Al-Mo alloys as rolled and annealed

An alloy of aluminum with tungsten, most probably containing some other metals, was patented and trade-named under the name of partinium; it probably was never actually manufactured.

An old patent issued in 1892 mentions for casting purposes an Al alloy containing 12% Mg and 12% W, which is evidently only a fake. In times more recent a patent was granted for the manufacture of an aluminum-copper-tungsten alloy by the method of treating a molten alloy of Al and Cu with sodium or potassium tungstate. Even the patentees did not claim to be able to introduce more than a fraction of a percent of W in this way, and the value of this addition can be positively denied.

The possibility of using small amounts of tungsten for the hardening of aluminum and aluminum-copper compositions was



recently studied by Whitmore and Sisco. They succeeded in introducing about 1% tungsten in an alloy with 10% copper, but found no improvement either in the cast or in a slightly heat-treated state. Strength figures obtained by these investigators show this alloy to have a tensile strength of 23,000 lbs. at 315° C. The authors themselves do not hold this figure to be spectacular; we believe however that this strength at 315° C. is almost unattainable in any other alloy.

### THE ALUMINUM NICKEL SERIES

This system was also investigated by Gwyer (Z. An. Ch., 1908, vol. 57, p. 113). The constitutional diagram looks like a replica of that of the aluminum-cobalt series, with some

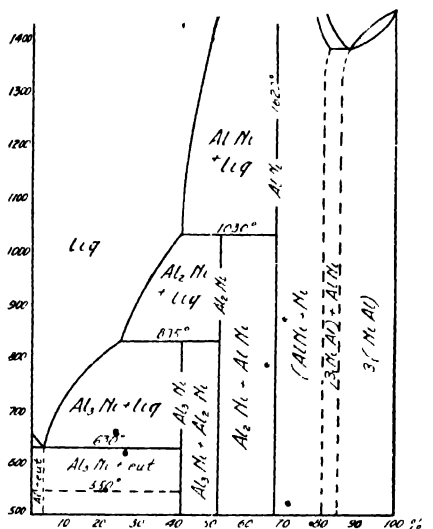


FIG. 41. Const-l diagram of the Al-Ni series by Gwyer.

(Z. An. Ch., 1908, v. 57, p. 113.)

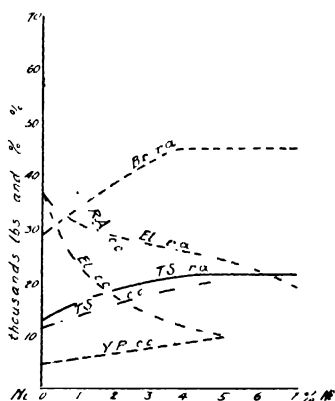


FIG. 42. Mechanical properties of the Al-Ni series

variations introduced from the aluminum-copper series. (Fig. 41.) Here, we have a compound, AlNi, melting at 1620° and able to retain quite an amount of nickel in its lattice thus forming a field of solid solutions from 67 to about 80% nickel.

Nickel itself can retain up to 16% aluminum in the form of solid solution and quite a number of valuable alloys might be found at the nickel end, one of them being aludel (containing about 3% aluminum) which is used for thermocouples. In the field from 0 to 67% nickel, we have two different compounds,  $\text{Al}_2\text{Ni}$  and  $\text{Al}_3\text{Ni}$ , which form peritectically from the compound higher in nickel interacting with the remaining liquid. The compound,  $\text{Al}_3\text{Ni}$ , forms a eutectic with aluminum, in which aluminum crystallizes primarily only below a content of 4 to 5% nickel. Even with higher amounts of nickel the melting curve rises quite gradually and it does not take more than 735° C. to form a homogenous liquid containing 10% aluminum. Under regular foundry practice, up to 15% nickel can be introduced with comparative ease, particularly if an auxiliary alloy containing say 30% nickel is used.

The electrical properties of the aluminum-nickel series were studied by Broniewski (An. Ph. & Ch., 1912, p. 5). He could not study alloys in the interval from 45 to 83% nickel, due to their high melting point and comparative brittleness. The curves which he obtained for the aluminum end of the diagram corroborate the presence of the  $\text{Al}_3\text{Ni}$  compound. They show also how nickel decreases the electric conductivity of aluminum and its temperature factor. It can be said that aluminum actually does not form any solid solutions with nickel while it definitely strengthens the alloy in a purely mechanical way. Up to 5% nickel the electric conductivity is not diminished by more than about 3%, whence nickel might be considered a very good (probably the best) addition to aluminum intended to be used for electric cables. Nickel up to 42% does not reduce the electrochemical potential of aluminum (Fig. 43).

The presence of nickel decidedly increases the strength of aluminum either in the cast or in the rolled state (Fig. 42). In the chill-cast metal, up to 5% and more can be introduced, with an almost directly proportional increase in strength and yield point. At about 5% nickel, we have a strength of 21,000 pounds per square inch, and a yield point of 10,000 pounds

in chill castings; elongation remains 10% and is sufficiently good for any purpose where castings are used.

The properties of the sand-cast alloys seem never to have been studied in a systematic way and no graphs for the properties can be shown. Still, we may remember that the first aluminum alloys used for sand casting in the United States contained about 6% nickel, "alloy No. 12." Aluminum-

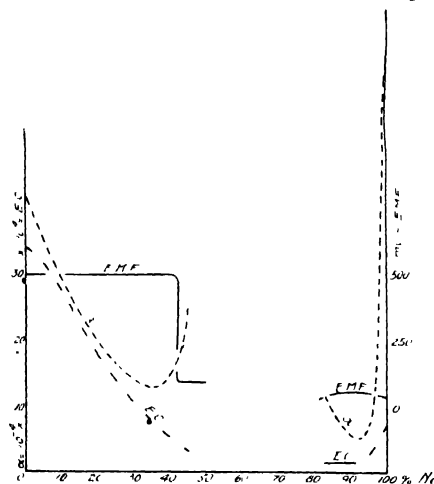


FIG. 43. Electric properties of Al-Ni series by Bronievski (An. Ph & Ch. 1012 p. 5)

nickel alloys of this composition in the cast form are decidedly stronger than aluminum-copper alloys; they are easily machinable and have other valuable properties. Nevertheless they are more difficult to make and more expensive than the aluminum-copper alloys which have superseded them in this country.

Nickel also forms very valuable aluminum alloys for the rolling mill; with 4% Ni we obtain in annealed sheets an ultimate strength of 22,000 pounds, Brinell hardness of 45, and elongation of 26%.

Alloys containing only aluminum and nickel are not frequently used, but composite alloys containing both copper and nickel are greatly favored for any work where high strength

at higher than normal temperatures is needed. The amount of nickel added is seldom over 2.5%.

The addition of Ni to aluminum is mentioned in five U. S. patents.

## ALLOYS OF ALUMINUM WITH PHOSPHORUS, SULPHUR, SELENIUM, TELLURIUM

Alloys of aluminum with the first mentioned element are interesting from two viewpoints: first, the possibility of obtaining better castings by the introduction of phosphorus as a deoxidizer; second, the possibility that phosphorus may prove detrimental to aluminum alloys.

A number of old patents actually stipulate additions of phosphorus to aluminum in casting alloys. At present, it is rarely attempted to use phosphorus as a deoxidizer, due to the simple fact that no element can effectively act as such in aluminum alloys. Regarding the possible detrimental influence of phosphorus, experiments by Czochralski have shown that quantities of phosphorus may be brought in contact with overheated liquid aluminum without remaining in the metal beyond traces, as neither aluminum phosphide nor any other metallic phosphide is actually soluble in liquid aluminum. Ingots which had been treated with phosphorus did not show more than 0.2% of the latter, and even this was confined to a segregation at the top of the ingot and in the pipe. These traces do not affect at all the mechanical properties of the finished sheets or rods. The observation of Czochralski that aluminum and its phosphide are practically unmixible in liquid state makes it useless to attempt further conclusions as to the aluminum-phosphorus diagram.

The mutual relationship of aluminum and sulphur is quite analogous to that of aluminum and phosphorus. Of course nobody would think of using sulphur as an additional element for aluminum; to the contrary, opinions have been expressed that sulphur might be quite detrimental to aluminum, based on the presence of aluminum sulphide,  $\text{Al}_2\text{S}_3$ . Experiments

by Czochralski have shown that aluminum sulphide is not retained by liquid aluminum to any important degree, and such traces as might remain in aluminum do not affect the properties of the alloys at all, at least not in wrought condition.

Selenium, being quite analogous to sulphur, should also have no desirable influence upon aluminum; on the other hand, the chance of meeting it in the foundry is practically nil, which renders it unnecessary to experiment with aluminum-selenium.

Tellurium, being an element with rather pronounced metallic properties, might be thought to prove valuable to some extent as an addition to aluminum or its alloys. The most recent experiments by F. Sisco and N. Whitmore (*Jour. Ind. & Eng. Chem.* 1924, p. 838) have shown that aluminum forms a compound with tellurium and that this compound is entirely insoluble in liquid aluminum. We can therefore conclude that neither phosphorus, nor sulphur, selenium nor tellurium are actually alloyable with aluminum and cannot affect its properties to any degree in the wrought state. In the cast conditions their compounds with aluminum will doubtlessly segregate and form weak spots.

#### ALLOYS OF ALUMINUM WITH PLATINUM, IRIIDIUM, RHODIUM AND PALLADIUM

The high price of these four metals entirely precludes their commercial use as additions to aluminum; nevertheless, iridium and platinum have actually been mentioned as desirable additional elements in aluminum alloys.

Constitutional diagrams of these alloys are not known, except that of the aluminum-platinum series which was studied by Chourigine (*R. Met.*, 1912). His investigation, however, did not relate to technical properties but only to the constitution of the series. Working with very small samples, Chourigine did not obtain very reliable results even with respect to the constitutional diagram; they are represented in Fig. 44 by heavy lines. This includes the liquidus up to 80% platinum,

the eutectic isotherm up to approximately 44% platinum, and a peritectic isotherm running from 40 to 70% platinum. Near the platinum end of the series Chourigine obtained no figures, as he evidently could not use platinum thermocouples for the high temperatures encountered.

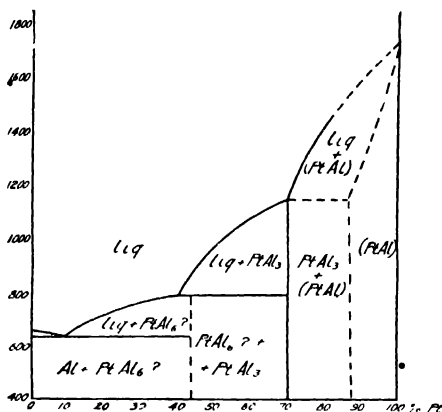


FIG 44 Const-l diagram of Al-Pt series

(Chourigine, Rev. Met., 1012, v. 9, p. 874-883).

By analogy with other series we may expect aluminum to form a solid solution in platinum, the latter including hardly over 12% aluminum by weight. Of the compounds found by Chourigine, one, namely  $\text{PtAl}_3$ , can have no technical importance, while another, probably  $\text{PtAl}_6$ , is the one which forms a eutectic mixture with aluminum. The physical affinity of platinum to aluminum is very high and platinum dissolves in aluminum quite rapidly in spite of the large difference in the temperatures of melting. Nothing is known as to the formation of solid solutions of platinum in aluminum.

#### THE ALUMINUM-ANTIMONY SERIES (Al-Sb)

Alloys of these two elements have been quite frequently investigated as to their constitutional diagram. The results of the first investigations could not be brought into accord with

the laws of thermodynamics. It was found, for example, that the liquidus curve rises very steeply from both pure aluminum and pure antimony melting points, indicating that a compound or compounds are being formed. The liquidus curve, as known in the past (Fig. 45, dotted line), has two flat maxima which do not correspond to a compound of a definite

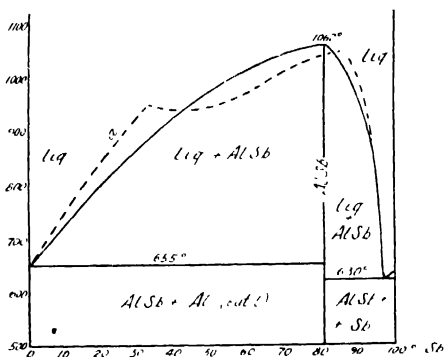


FIG. 45 Const-t diagram of Al-Sb series by Urasov  
(J. R. Ph. Ch. S., 1919, v. 51, p. 461)

composition. The structures of alloys corresponding to these maxima were never found to be homogenous either at one definite point or in a range of compositions. No eutectic isotherm was found between the two maxima. On the other hand, one definite eutectic line was observed beginning at pure aluminum and ending somewhere in the central part of the field, and another beginning with pure antimony and also ending near the same field.

The most recent investigation by Urasov has shown that aluminum and antimony form only one compound, AlSb, the velocity of the formation of this compound being rather low in spite of the fact that it does not dissociate much on melting. By holding an alloy with a composition near that of AlSb for a long time at a temperature of  $1100^{\circ}$ , Urasov was able to make the metals combine practically completely, and in this way he obtained a definite compound with a definite melting point at  $1062^{\circ}$ . This compound crystallizes primarily from any alumi-

num-antimony alloy, both pure metals crystallizing eutectically. No solid solutions of any kind were discovered at the aluminum end of the series and the primary crystals of the Al-Sb compound were found to be quite brittle.

In spite of the presence of this brittle compound, aluminum-antimony alloys with antimony up to 7% may be rolled hot and cold without much trouble. The rolling process may be pushed even to 10.5 antimony, but beyond that rolling is no longer successful. The brittleness of the compound AlSb robs it of any value as a hardener of aluminum; antimony not only fails to improve the strength and hardness of the rolled and annealed alloy, but it also has an adverse effect on ductility (according to Schirmeister).

It is rather improbable that antimony should have any value in alloys used for casting. Still seven U. S. Patents mention it as an alloying element for aluminum, mostly in connection with comparatively large amounts of copper and zinc. Only one patent (No. 1453928), issued quite recently, mentions an addition of 1 to 1.5% antimony as the only alloying elements, while another cites it as an addition to aluminum-silicon alloys of the Alpax type.

Recently the author found that by alloying antimony in amounts of 15-20% with aluminum and silicon (10% of the latter) a product results which after a heat treatment at 500° for 6 h. shows fair sized grains of AlSb evenly distributed in a eutectical matrix of Al-Si. In this state the alloy resists compression better than plain Al-Si and has a sufficient ductility. The moderately hard and uniformly distributed grains of AlSb lend the alloy the structure and probably also bearing properties not obtainable in other alloys of aluminum base.

Nothing is known about the electrical properties and chemical stability either of the series as a whole, or of aluminum to which small percentages of antimony has been added.



## THE ALUMINUM-SILICON SERIES (Al-Si)

This was first investigated reliably by Fraenkel in 1908 (*Z. An. Ch.*, vol. 58, p. 154). This author found it to be a purely eutectiferous system with no compounds and practically no solid solutions on the aluminum side. The eutectic composition was considered to lie at 10.5% silicon and at a temperature of about 578 C. More recent investigations have shown that there are ranges of solid solution at both the aluminum and the silicon ends of the series (Fig. 46). Solid alumi-

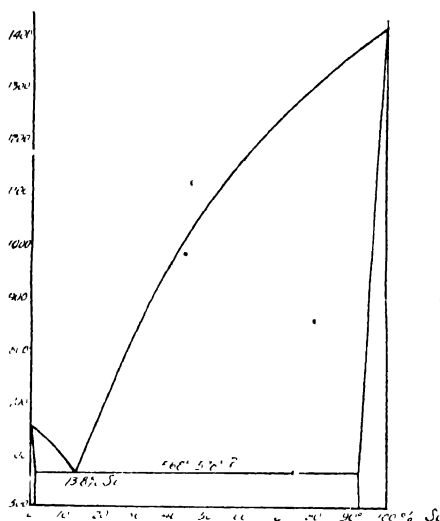


FIG. 46 Constl diagram of the Al-Si series by Fraenkel.

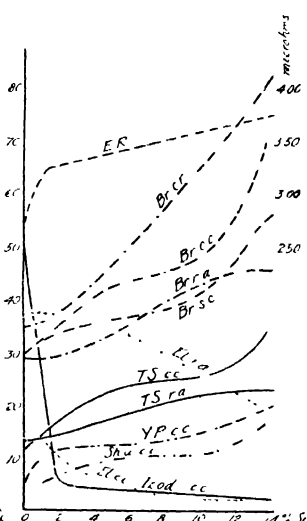


FIG. 47 Mech properties of the Al-Si series

num is able to retain in its lattice about 1.5% silicon by weight in the completely equilibrated state. In casting practice this equilibrium is rarely reached and more than 0.7% silicon seldom remains in the solid solution. The eutectic formed under normal conditions, according to Fraenkel, is generally rough, the silicon being present in the form of long needles and plates. As soon as the eutectic point is passed, silicon crystallizes primarily, forming large hexagonal plates. Alloys containing the normal eutectics or an excess of the hexagonal

grains of silicon do not show very good mechanical properties; in particular they have a very low impact resistance and almost no ductility at quite small amounts of silicon. The fractures of such alloys, whether furnace-cooled or sand-cast, are rough and gray crystalline.

About 1921, it was discovered by A. Pacz that the structure may be modified by treating the molten alloy with sodium fluoride or sodium hydroxide at a temperature approximating 800 to 850°. The modifying treatment results in an extensive refinement of the silicon grainlets, in every alloy below 13.5% silicon, while at 14% silicon approximately a very fine, uniform eutectic structure results, which can be preserved under favorable conditions through the whole range from 13.5% to 17% silicon. The refined eutectic has remarkably excellent mechanical properties, making it possible to obtain castings with very high strength, good impact resistance, and a ductility not obtainable in other aluminum alloys with so high a proportion of added metal. In fact, aluminum-silicon alloys, if treated in the manner described, are practically the only true eutectical binary alloys of aluminum. The same modification of structure is obtainable by treating the molten charge with sodium in amounts of 0.1% of the total weight of the charge as discovered by the Aluminum Company of America. The British Aluminum Company found that small amounts of calcium act almost identically.

Many explanations of the modifying process have been offered. The first was that sodium fluoride or sodium hydroxide dissolves the oxides of aluminum or silicon or both, bringing aluminum and silicon into much closer contact, and thus shifting the eutectic composition and temperature. This explanation seems improbable, since the elimination of rather small amounts of unevenly distributed aluminum oxides with the help of still more unevenly distributed sodium compounds is hard to imagine. A much better explanation is that, in the range of temperatures closely adjacent to the eutectic isotherm, additions of sodium metal in some purely physical manner may introduce certain changes in the fluidity, internal friction, or

surface tension of the melt, or in the crystallizing power of both aluminum and silicon. Furthermore, it is quite possible that the presence of sodium or of any alkaline metal changes the proportions of differently condensed liquid molecules and causes deviations of the osmotic pressure of silicon from that which prevails under ordinary conditions.

The question of the solid solubility of silicon in aluminum was recently studied in detail by S. Daniels of the U. S. Air Service. He established once more the fact that there are practically no alloy series where the solid solubility runs stationary through the whole range of temperatures. Near the melting point of the Al-Si eutectic, this solid solubility runs well into 2% while it decreases at lower temperatures. Either a plain anneal or a quench-ageing process leads to a profound change in structure. The network structure of the cast metal disappears, and any excess of silicon either deposited primarily or precipitated from the solid solution coagulates. The change due to quench-ageing does not affect either the hardness or strength of the cast metal, enhances, however, the ductility to a very strong degree. On the other hand, low silicon alloys were found by Daniels to be somewhat subject to warping in heat treatment. A plain anneal at high temperature drops the strength almost to that of pure aluminum.

The mechanical properties of the sand-cast and heat-treated but non-modified Al-Si alloys up to 5% Si are represented in Fig. 47a.

Among the properties of aluminum-silicon alloys we must distinguish those which change continuously with the addition of silicon from those which do not follow any continuous law. The chemical resistance of aluminum-silicon in the cast state, which is higher than that of practically all other aluminum alloys in the cast form, increases continuously, both the normal and the modified eutectics having an increased chemical resistance. Electric resistivity varies in the same way. The mechanical properties, however, do not follow a simple law in the cast state. A small strengthening occurs with the first 1 or 2% of silicon, after which the properties change but

slightly up to the immediate vicinity of the eutectic composition, where every mechanical property shows a peak (Fig. 47).

It is the mechanical properties of aluminum-silicon alloys that are most important to both manufacturer and user. The success of aluminum-silicon casting does not depend so much upon cleanliness and good control of the melting and casting operations as upon a very careful attention to the uniform attainment of the modified eutectic composition. The latter

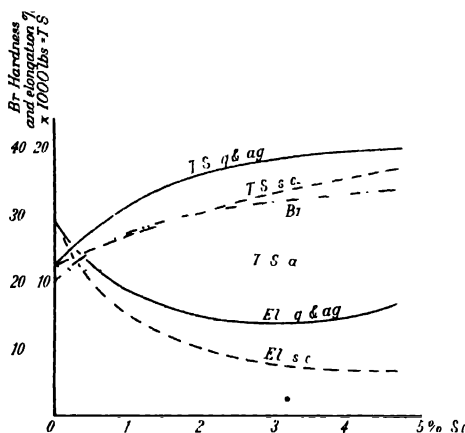


FIG. 47a Influence of small additions of silicon upon mechanical properties of sand cast aluminum. Idealized form of data by S. Daniels.

cannot be obtained with less than 13% silicon and even at this composition it is quite possible simultaneously to produce white patches of aluminum and a number of large grains of silicon if cooling from the temperature of the modifying treatment to the temperature of pouring occupies too long a time. The best results, *i.e.*, a most uniform eutectic structure, are obtainable with no less than 14 to 15% silicon, on the other hand slight variations in the operating routine lead, for reasons not yet understood, to a precipitation of large grains of elementary silicon and a consequent inferiority of the casting. The production of aluminum-silicon alloys for castings is thus a delicate operation, but its results are unattainable in any other

way. The constancy in the strength of "alpax" or "silumin" alloy (the eutectic composition in the modified form) up to 200° C. is particularly advantageous. This alloy likewise shows a minimum tendency to crack at places where sections change in thickness, and around the cores.

The best operating condition for the production of superior alpax castings, calls for a generous use of chills, which help to keep the primary crystallization of silicon at the minimum. By this method it is possible to obtain strengths up to 35,000–38,000 lbs., and yield points of 15,000 lbs. However, it is safer not to expect more than 30,000 and 12,000 lbs, respectively, under the best average conditions.

#### THE ALUMINUM-TIN SERIES (Al-Sn)

This was investigated first by Anderson and Lean (Proc. Royal Soc., 1902, p. 277). In those times, however, the theory of constitutional diagrams was not well developed; whence the thermic observations made by these authorities really afforded no explanation pertaining to the complete solidifying process. A later investigation by Gwyer (Z. An. Ch., 1906, vol. 49, p. 311) led him to believe that while the liquidus was traced by Anderson and Lean with substantial accuracy, the actual solidus is represented only by a eutectic line running through the whole diagram from practically pure tin to practically pure aluminum (Fig. 48). This explanation by Gwyer fits well with the results of Schirmeister's investigation of the mechanical properties of aluminum-tin alloys in the rolled and annealed state (Fig. 49). The latter found that hot rolling is impossible with these alloys, at least with those containing substantial quantities of tin, this being due to the melting of the film of eutectic tin surrounding the grains of aluminum. On the other hand, the undoubted increase in ultimate strength in the rolled and annealed state, as compared to pure Al (Fig. 4), could hardly be attributed to the mere presence of eutectic tin; it might be much better accounted for by the assumption that

some tin was retained by aluminum to form a solid solution. Neither Gwyer nor Anderson and Lean investigated this series micrographically with sufficient completeness.

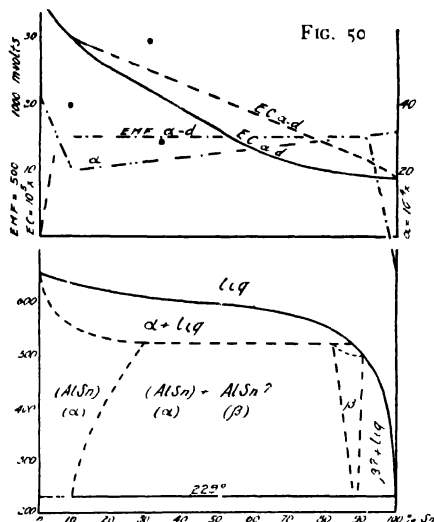


FIG 48 Const-t diagram of Al-Sn series by Gwyer.

(Z. An. Ch., 1906, v. 49, p. 311.)

FIG 50. Electric properties of Al-Sn series.

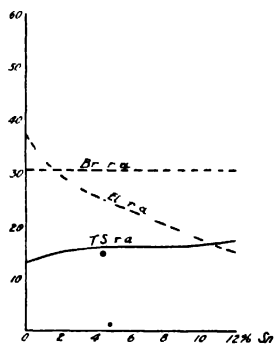


FIG 49 Mechanical properties by Schirmeister.

(Rev. de. Met., 1915)

(The dotted line in the const-t diagram represents an interpretation, by the author, of the results obtained by Anderson & Lean (Proc Royal Soc., 1903, p. 277).)

Experiments by Broniewski, who investigated the electrical properties of this system in 1912 with results which are represented in Fig. 50, also can hardly be explained on the theory of a plain eutectiferous series. Another fact is that alloys high in tin exhibit a strong tendency to disintegrate under the action of moist air or water, while alloys low in tin do not show this tendency at all. On the basis of these facts we have tried to interpret the second breaks in the cooling curves as observed by Anderson-Lean in such a way as to explain the mechanical and chemical properties of the aluminum-tin alloys. It seems probable (follow the dotted line in the diagram)

is somewhat analogous to titanium and iron on one side and to chromium, nickel and cobalt on the other, we suggest the following diagram (Fig. 53), as hypothetically representing the probable conditions. At least at the aluminum corner of the diagram and up to 30% vanadium, its general shape and the direction of the liquidus must represent very nearly the actual facts. The dotted line at the top of the diagram shows the approximate hypothetical variation of hardness in this system, the highest point being assumed at 600 Brinell.

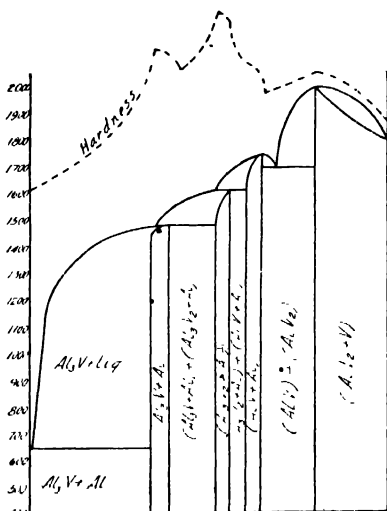


FIG. 53. Const-1 diagram of the Al-V series, developed by the author from data by N. Czako (C. R., v. 156, p. 140.)

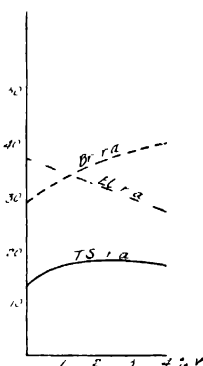


FIG. 54. Mech properties of Al-V alloys as rolled and annealed

The physical properties of aluminum-vanadium alloys were never subjected to a study except the slight amount of work by Schirmeister, as represented by Fig. 53. According to the latter, 2% vanadium added to aluminum affords a substantial increase in strength in the rolled and annealed alloy, coupled with just as substantial an increase in hardness. The percentage elongation of the annealed alloys drops almost in a straight line, but even at 4% vanadium it is sufficiently high for any purpose.

Vanadium is only once mentioned in a U. S. patent relating to aluminum and even there its amount and manner of action is not specified.

### THE ALUMINUM-ZINC SERIES (Al-Zn)

This has been investigated very frequently from the viewpoint of constitution. The most recent investigations were carried out in Japan by T. Tanabe (J. Inst. Met., 1924, vol. 32), and by Hansen Gayler (J. Inst. Met., 1922, vol. 27, p. 267).

The diagrams developed by these investigators do not differ to any noticeable extent (Figs. 55, 56). Both found that aluminum and zinc form a compound with the formula  $Zn_3Al_2$  which decomposes on melting at  $445^\circ$ . On freezing, it

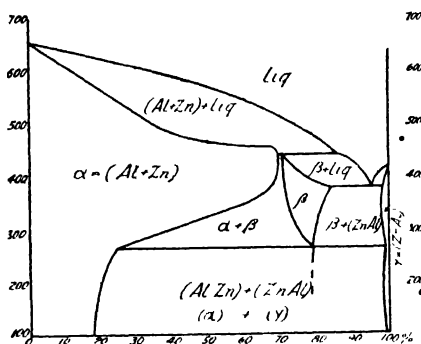


FIG. 55. Const-I diagram of the Al-Zn series by T. Tanabe. (J. I. M., 1924 (XXXII) )

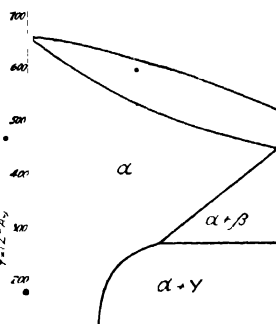


FIG. 56. Al-Zn diagram by Hanson & Gayler (J. I. M., 1922 (XXVII), p. 267.)

may retain quite large quantities of either aluminum or zinc in solid solution, but finally undergoes a eutectoidal breakdown at about  $270^\circ$  C. The products of the dissociation are: (1) a very rich solid solution of zinc in aluminum; (2) a solid solution of aluminum in zinc containing no more than 1.5% aluminum. Accordingly, at normal temperature we have only two different phases: a solid solution of zinc in aluminum



saturated at about 17% zinc, and a saturated solution of aluminum (1.5% Al) in zinc. At high temperatures we have three phases: (1) a zinc-aluminum solid solution very rich in zinc; (2) a solid solution of aluminum or zinc in the compound  $\text{Al}_2\text{Zn}_3$ ; (3) a solid solution of aluminum in zinc. Alloys up to 17% zinc, whether slowly cooled or worked and annealed, represent only a uniform solid solution. Those richer in zinc undergo a continuous transformation with the precipitation of the compound at higher (over  $270^\circ$ ), or of the zinc phase at lower temperatures.

Most recently the Al-Zn diagram was reinvestigated by Ishihara of the Tohoku Imperial University. Using rather refined methods he was able to ascribe more correct positions for the boundaries of the different fields, and found also certain complications in the mechanism of the transformations within this series. In general, however, his diagram coincides completely with that of Tanabe.<sup>1</sup>

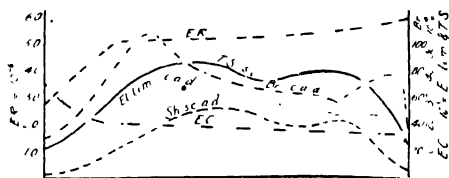


FIG. 57. Electrical and other physical properties of Al-Zn series.

The electrical and mechanical properties of the aluminum-zinc alloys are given in Figs. 57, 58, 59. It must be pointed out that the ultimate strength of the alloys increases continuously with the addition of zinc, both in the cast and the wrought state, as common to all solid-solution alloys. Ductility is not affected in the hot rolled or in the annealed state.

Alloys containing from 20 to 25% zinc should be particularly good for castings, due to their high ultimate strength and high yield point in the sand-cast condition. In wrought alloys, 20% zinc is practically the limit. The alloys with 30% zinc are hardest of the series and also have the highest elasticity limit.

<sup>1</sup> For new information on aluminum zinc alloys see Appendix.

The variation of the saturation limit of the aluminum-zinc solid solution with temperature makes it possible to heat-treat aluminum-zinc alloys. Thus, up to 60% zinc an alloy can be heated to about 425° C., furnace soaked to make it uniform, and quenched, in which condition it retains the high zinc content of the solid solution. Alloys thus heat-treated undergo a

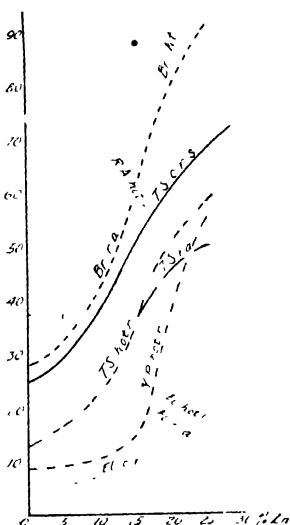


FIG. 58. Mechanical properties of wrought Al-Zn alloys.

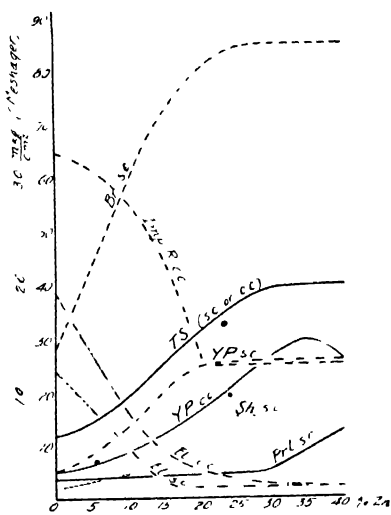


FIG. 59. Mechanical properties of cast Al-Zn alloys by Rosenham & Archbutt (Inst Mech Engineers, 1912), also Portevin.

(R. Met., 1911, p. 721)

very rapid ageing, the compound  $Al_2Zn$ , precipitating in a very fine form and strengthening the alloy (making it harder and giving it higher tensile strength). Unfortunately, this condition cannot be preserved indefinitely, as the precipitated compound undergoes a eutectoidal transformation during which the zinc phase crystallizes and the hardness drops again; ageing of quenched aluminum-zinc alloys therefore does not yield the same valuable effect as to strength and hardness that is observed in some other alloys of aluminum. Furthermore, quenching and ageing are of no help to ductility; the elongation falls below that of the worked and annealed metal.

Alloys high in zinc and containing beta (the second phase) at higher temperatures also undergo a process of ageing after quenching after which the eutectoid is precipitated in a very fine form. The latter is very unstable and the hardness acquired in the first hours of ageing is lost comparatively rapidly due to the balling up of the grainlets of Al and Zn.

Alloys below 17% zinc cannot be altered by heat-treatment at all, as they always represent a uniform solid solution.<sup>1</sup>

Neither the worked alloys (up to 20% zinc) nor the cast ones (up to 30% zinc) are much utilized. Their high strength is not reliable and they exhibit strongly the property of season cracking. This is not, however, an actually demonstrated fact but simply a persistent opinion; it is rendered doubtful because the Al-Zn alloy of the 20% composition does not lose much strength even after a very prolonged anneal.

Patents have been issued in the United States for aluminum alloys containing up to 30% zinc for casting purposes and up to 16% zinc for rolling work. These alloys, however, are never binary but contain numerous other alloying metals.

The following features adversely affect the usefulness of the binary Al-Zn alloys for casting purposes. First, they retain the high shrinkage factor of pure aluminum until the amount of zinc added reaches 30%, when shrinkage is almost the same as with the 12% Al-Cu alloys (Fig. 60). Secondly, near their melting points they are exceedingly weak (like other alloys of the pure solid-solution type) and any obstacle to shrinkage produces cracks of the most varying shapes and dimensions, which may not be noticed until a good deal of machining has been done. Thirdly, the alloys with over 20% Zn, as cast either in sand or chills, are never in a state of equilibrium; this state is reached gradually by the disintegration of excess solid solution. The products of this disintegration having an average density greater than that of the cast metal, the resulting contraction ruins the usefulness of the castings.

Chemical properties of aluminum-zinc alloys are not positively known. It seems doubtful, however, that they can com-

<sup>1</sup> See Appendix.

pete with other casting and rolling alloys of aluminum, particularly those containing copper or silicon. Alloys with over 30% Zn are easily corrodible by plain tap water and more so by saline solutions.

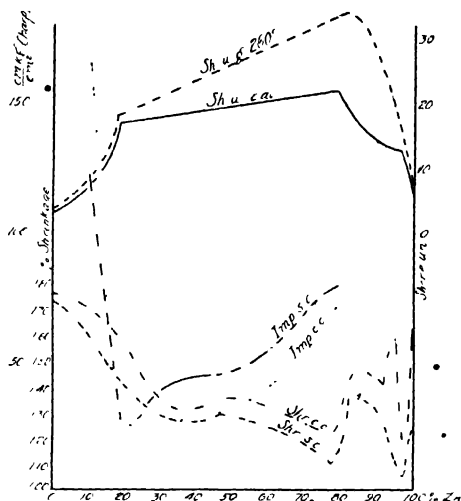


FIG. 60. Hardness and shrinkage of chill-cast and sand-cast Al-Zn alloys.

The effect of zinc in imparting strength to aluminum is much less pronounced than that of an equal amount of copper; nevertheless, a higher strength can be gained with zinc. As between an aluminum-zinc and an aluminum-copper alloy having the same mechanical properties, the zinc alloy is usually heavier, has a higher electrical resistance, and a somewhat lower thermal conductivity.

## THE TERNARY SYSTEMS OF ALUMINUM ALLOYS

The comparatively complicated nature of the constitutional diagram for every binary alloy of aluminum makes it extremely difficult to establish the constitutional diagrams for the ternary alloys. Only a few systems have been studied throughout the whole range of compositions, namely, alu-

minum-zinc-copper, aluminum-tin-copper, aluminum-nickel-copper, and aluminum-magnesium-zinc.<sup>1</sup> However, almost any constitutional diagram is based largely on a purely theoretical investigation which aims to account, in a general way, for the processes of solidification and transformation occurring in the system. The physicochemical details of constitution and the mechanical details of structure in the aluminum corners of the diagrams where practically all industrial light alloys are confined, were never completely investigated by the authors of the constitutional diagrams. Accordingly, our information on the above mentioned ternary systems has very little practical value. Only recently a few systems have been investigated thoroughly at the aluminum corners of the diagrams, the work being done almost exclusively by the members of the British National Physical Institute.

In a general way, we may consider the following possible cases of ternary aluminum alloys:

1. Both additional elements form compounds with aluminum and do not form them mutually. In this case undoubtedly both additions will be present in the form of aluminides as soon as their total amount exceeds the solid solubility limit at the normal temperature. Any combination of additions of copper, iron, nickel, cobalt, chromium or silver will act in this way. In a few of the mentioned combinations we can expect a ternary constituent (either a solid solution of two different aluminides or an actual ternary compound) to be present.

2. One of the additional elements forms compounds with aluminum while the other does not, but has a higher affinity for the first additional metal. This is the case of systems containing copper, iron, chromium, cobalt, or manganese on the one hand, and silicon on the other. Here we have to determine which combination would be more natural; that of a silicide of the first mentioned metals or of an aluminide. Silicon undoubtedly has a much stronger affinity for the heavy metals,

<sup>1</sup> The investigation of the aluminum-magnesium-copper system, by P. Vogel, up to 55% Mg and 54% Cu (*Zeits. an. ch.*, 1919, vol. 107, p. 265) and that of aluminum-copper-zinc by Jares (*Zeits. für Metallkunde*, 1910, vol. 10, p. 11) must be mentioned as elaborate studies of the constitutional diagrams.

at high temperatures, than aluminum. Accordingly, we should expect the predominance of silicides so long as the total silicon is not combined. The simultaneous presence of crystals of aluminum, silicon, silicide, and aluminide cannot occur, however, as this would be absolutely contrary to the phase rule. The actual conditions may be determined in the following manner: In the triangular ternary diagram we draw two cross-sections, one connecting the aluminum corner with the most stable silicide composition of the other metal, and the other connecting the silicon corner with the aluminide highest in aluminum. (Fig. 61.)

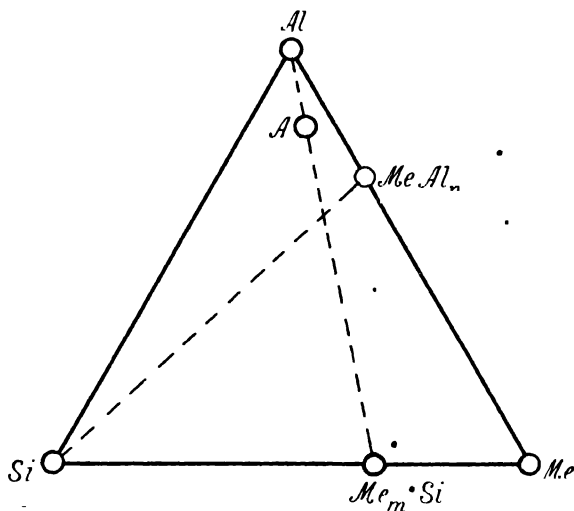


FIG. 61.  $MeAl_n$  — The aluminum richest compound of the metal "Me"

$Me_mSi$  — The silicon poorest compound of the metal "Me."

A — A high aluminum ternary alloy which may consist structurally of either  $Al + Me_mSi$  or  $Al + MeAl_n + Si$ .

By studying a few alloys with compositions along these lines we find whether the structure remains binary (pseudo binary) or becomes ternary. The line along which the first occurs is the line of stable conditions; it appears (although never sufficiently investigated) that, with the whole mentioned group of metals in the presence of aluminum and small

amounts of silicon, the stable line runs at normal temperatures from silicon to the corresponding aluminides. Accordingly, we find the alloys always to contain aluminum, aluminide, and silicon.

It is, however, quite possible that at high temperatures, particularly in the liquid state, the silicides are more stable and disappear only through a reaction with aluminum at lower temperatures. For this reason we might expect the appearance of silicides in alloys which did not have enough time to become chemically balanced, *i.e.*, chill-cast and, to a certain degree, sand-cast. This is how we might explain why the simultaneous presence of such metals as iron, cobalt, or chromium with silicon acts adversely on the mechanical properties of the technical aluminum-silicon alloys.

Another explanation suggests that at certain contents of the first additional metal and of silicon a ternary compound is formed, the presence of which is detrimental to the castings. In alloys containing iron and silicon this ternary compound forming long thin prismatic bodies is called the constituent X.

2a. A different case is found in the aluminum-magnesium-silicon system, and probably in aluminum-calcium-silicon. Here the line aluminum—magnesium silicide (or calcium silicide) is the stable one, and as long as there is an excess of either magnesium or silicon, the compound  $Mg_2Si$  is formed exclusively and the element in excess may either remain free (in case of silicon) or may form a compound with aluminum (in case of magnesium).

3. The next case is when the two additional metals present might mutually form a compound but only one of them forms a compound with aluminum. This group will embrace silver, copper, nickel, manganese, cobalt, and chromium on the one hand, and zinc and tin on the other. Here the affinity between the two additional metals is comparatively slight as compared with that between aluminum and the first additional metal. Therefore, and due to the excess of aluminum, we find aluminides of the first addition, while the second metal, zinc or tin, remains in a free state as long as its content is beyond the

limits of solid solubility in aluminum in the presence of the other metal.

3a. However, if magnesium (and probably calcium) is the first additional metal, then its affinity to zinc (and possibly tin) proves much stronger than that between magnesium and aluminum, and either magnesium or zinc will be exhausted in the formation of the compound  $\text{MgZn}_2$  before the excess metals can form new constituents. Of course, to a certain limit, the metals may both go into a solid solution in aluminum.

4. In the case where the additional metals form compounds mutually, and also with aluminum, we have the most complicated conditions. However, this may happen only in the presence of molybdenum or tungsten as the second additional metal. Thus, in the simultaneous presence of nickel and molybdenum, or of cobalt and tungsten, for instance, we would not know which constituent might appear in the alloy, and we have not enough facts even to venture a preliminary opinion on this subject.

## THE ALUMINUM-MAGNESIUM-SILICON SYSTEM

This series was investigated by Hanson and Gayler (J. Inst. Met., 1921, vol. 26, p. 321). The diagram, Figs. 62a, b, c, d, show the steps in the cooling of alloys containing up to 10.5% silicon<sup>1</sup> and 13% magnesium. We have (62a) the surfaces of the primary crystallization; one representing the solidification of a solid solution of silicon, and magnesium in aluminum, while the adjoining surfaces represent the crystallization of  $\text{Si}$ ,  $\text{Mg}_2\text{Al}_3$  and  $\text{Mg}_2\text{Si}$  respectively. Going below these surfaces (Fig. 62b) we find those of the secondary crystallization. At the aluminum corner we see a comparatively large field of the uniform "alpha" solid solution while the adjoining surfaces represent the variable binary crystallizations of  $\alpha + \text{Si}$ ,  $\alpha + \text{Mg}_2\text{Si}$  and  $\alpha + \text{Al}_3\text{Mg}_2$ .

<sup>1</sup> Formerly accepted as the eutectic composition of the Al-Si series. Now this point has to be shifted to 13.8% Si.



Next, we have complete solidification at approximately  $450^{\circ}$ , when the composition diagram is divided into the following fields (Fig. 62c):

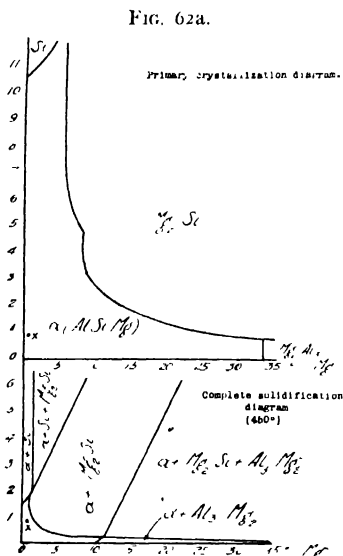


FIG. 62c

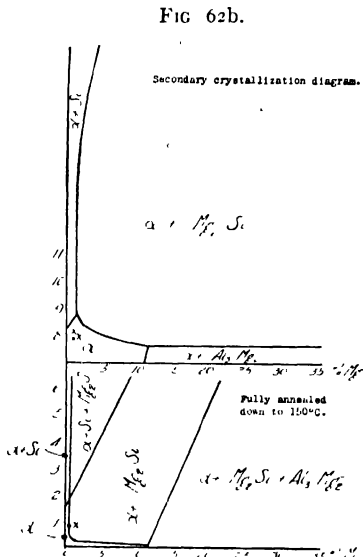


FIG. 62d.

FIG. 62 Partial ternary diagram of the Al-Mg-Si system.

By Hanson & Gayler. (J. I. M., 1921, v. 26, 321)

(1) The monophase field of homogenous alpha with the adjoining binary fields of alpha + Si, alpha +  $Mg_2Si$  and alpha +  $Al_3Mg_2$ . These fields of binary structures are separated by two fields of ternary structures, one containing alpha + Si +  $Mg_2Si$ , and another alpha +  $Mg_2Si$  +  $Al_3Mg_2$ . Finally, in the completely annealed state at say  $150^{\circ}C.$ , we find the same fields with the only difference that the field of homogenous alpha narrows down to a small, angular belt. The binary fields of alpha + silicon and alpha +  $Al_3Mg_2$  narrow down almost to extinction, while the ternary fields increase in size just as does the binary field, alpha +  $Mg_2Si$ .

The purpose of this investigation by Hanson and Gayler was to elucidate the mechanism by which the field of homogenous alpha, as saturated right after the completed solidifica-

tion narrows down with the precipitation of crystalline  $\text{Mg}_2\text{Si}$ . The above described structural details found by these authors show us sufficiently well what happens on quenching and heat-treatment of aluminum containing slight amounts of magnesium and silicon. In fact, additional experiments by Hanson and Gayler concerning the changes in hardness and ultimate strength in this system have shown that aluminum containing magnesium and silicon is actually amenable to heat treatment, resulting in a great improvement of its mechanical properties. The same processes account mainly for any improvement obtained by the heat-treatment of aluminum alloys containing sufficient amounts of magnesium.

Besides investigating the aluminum corner of the system Al-Mg-Si in general, the same authors established the constitutional diagram of the pseudo-binary series, Al- $\text{Mg}_{12}\text{Si}$  (Fig. 63)

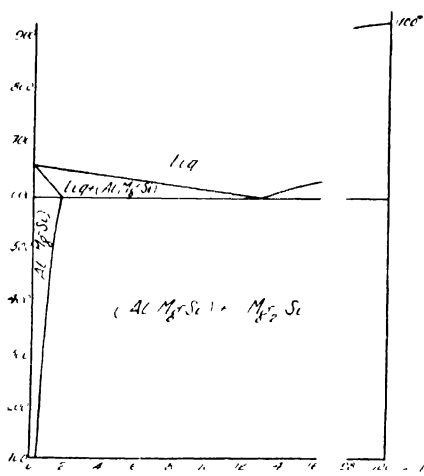


FIG. 63. Const-l diagram of the pseudo-binary series Al- $\text{Mg}_{12}\text{Si}$ .  
By D. Hanson & M. Gayler.  
(J. I. M., 1921, v 26, p. 321)

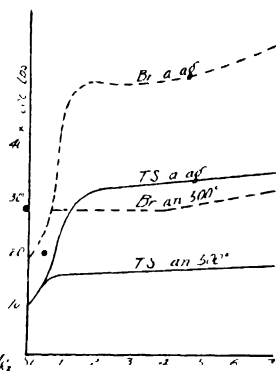


FIG. 64. Strength and hardness of the Al- $\text{Mg}_{12}\text{Si}$  alloys in the rolled and heat-treated state

and the mechanical effects of heat-treatment as applied to this system (Fig. 64). This pseudo-binary series was found to be eutectiferous, with a eutectic at 12.5%  $\text{Mg}_2\text{Si}$  and at a temperature of  $590^\circ\text{C}$ ., and with a region of solid solutions

widening to about 2%  $\text{Mg}_2\text{Si}$  near the eutectic temperature and narrowing down to about 0.6% under normal conditions. The diagrams of mechanical properties in this system, as affected by quenching, are especially interesting.

The same investigators also studied the effects of excessive magnesium upon the constitution and properties at the aluminum corner of the diagram. In Fig. 65 we see that excess magnesium decreases the solubility of  $\text{Mg}_2\text{Si}$  both at the higher (heavy-line boundary at  $400^\circ$ ) and also at the lower tempera-

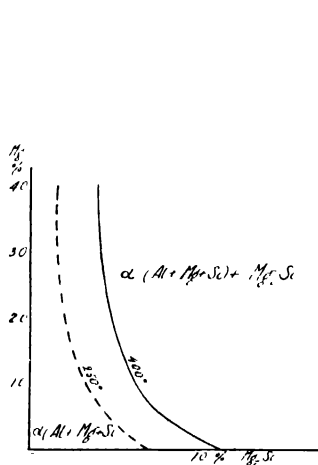


FIG. 65 Field boundaries in the ternary system Al-Mg- $\text{Mg}_2\text{Si}$

By Hanson & Gayler. (J. I. M., 1921, v. 26, p. 321.)

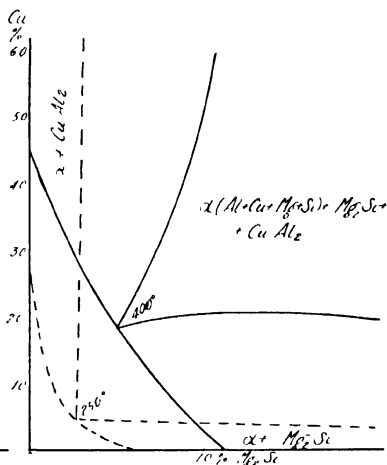


FIG. 66 Field boundaries in the ternary system Al +  $\text{Mg}_2\text{Si}$  + Cu

By M. Gayler. (J. I. M., 1922, v. 28, p. 213.)

tures (dotted line at  $200^\circ$ ). Now the hardening of the alloys by heat treatment is based upon two factors: first, the amount of  $\text{Mg}_2\text{Si}$  which can be brought into solid solution at higher temperatures, which amount is affected adversely by the presence of magnesium; second, the amount of  $\text{Mg}_2\text{Si}$  which will have to precipitate in ultra-microscopical form from the solid solution at lower temperatures, which is affected advantageously because the solid solubility at lower temperatures decreases quite rapidly in the presence of magnesium. Accord-

ingly, alloys containing a certain excess of magnesium (but not a very large one) must be more sensitive to heat treatment and produce better results. In fact, with regular aluminum containing about 0.4% to 0.6% silicon, the theoretical amount of magnesium necessary to produce a magnesium silicide would be 0.7%–1.05%, whereas additions of 1.2% to 1.5% magnesium are found to be the most suitable in making low-alloyed, heat-treated aluminum sheets and shapes of high strength.

### THE ALUMINUM-COPPER-MAGNESIUM SYSTEM

Another ternary system studied by Mary Gayler was that of aluminum-copper-magnesium at the aluminum corner of the series. The diagram represented in Fig. 67 shows (heavy

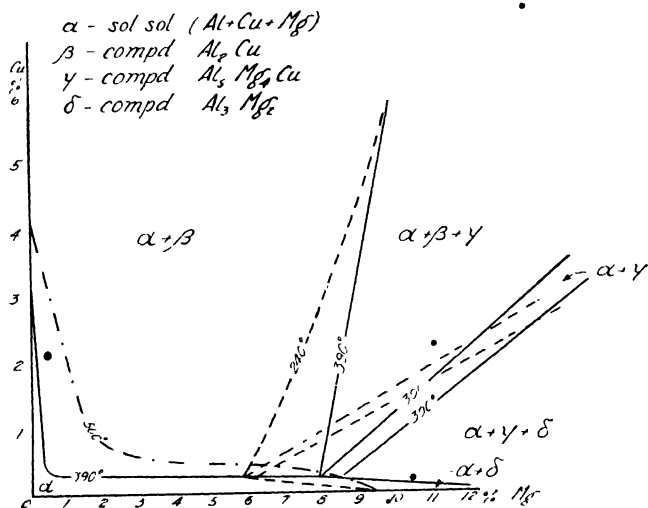


FIG. 67. Al-Cu-Mg diagram by Marie Gayler. (J. I. M., v. 20, 507.)

dotted line) the saturation limit of aluminum containing magnesium and copper simultaneously, while the full line at the left of it indicates how the same field is narrowed down at 390°. This field of solid solutions of varying saturation is

adjoined by three binary fields, the largest of them comprising the alpha solid solution and the "beta" or pure  $\text{Al}_2\text{Cu}$  compound. Another field of binary structures is very small and represents a narrow belt near the aluminum-magnesium line where we have alpha + delta, the latter being the compound  $\text{Al}_3\text{Mg}_2$ . There is still another belt which represents binary structures of alpha + gamma, which is either the ternary compound, presumably  $\text{Al}_3\text{Mg}_2\text{Cu}$ , or a double aluminide of a variable composition. Between the binary fields we have the ternary ones, composed of alpha + beta + gamma, and alpha + gamma + delta, respectively. The boundaries of these fields change considerably between the positions occupied at  $390^\circ$  and at  $240^\circ$ ; below the latter temperature the limits remain practically constant down to normal.

The variable saturation of the alpha field makes it possible, by saturating aluminum with a suitable amount of copper and magnesium at higher temperatures, and then quenching to preserve the solid solution in a super-saturated form at the lower temperatures. It was found, however, that alloys so composed do not show the whole benefit of heat-treatment and particularly do not age with sufficient regularity. The best properties are brought out only by a tempering at a comparatively high temperature, included between  $180^\circ$  and  $250^\circ \text{C}$ .

By the substitution of  $\text{Mg}_2\text{Si}$  for magnesium, Miss Gayler (Jour. Inst. Met., 1922, vol. 28, p. 230) obtained a pseudo-ternary diagram represented in Fig. 66, which shows how actively copper and magnesium silicide affect their mutual solubility at lower temperatures, and how comparatively large the same field is at a temperature of  $400^\circ$ . The heavy and the dotted lines in this figure represent the variations in the boundaries of the three structural binary fields, (1) alpha (homogenous solution of copper + magnesium + silicon in aluminum); (2) Alpha +  $\text{CuAl}_2$ ; (3) alpha +  $\text{Mg}_2\text{Si}$ ; and the ternary field; (4) alpha +  $\text{Mg}_2\text{Si}$  +  $\text{CuAl}_2$ . If, for instance, we have an alloy containing 0.6%  $\text{Mg}_2\text{Si}$  and 1.5% Cu it will undoubtedly represent a homogeneous solid solution at a temperature slightly above  $400^\circ$ , while at a temperature of

250° it will have a ternary structure of the field 4. By preserving the solid solution by quenching and disrupting it by ageing, we obtain the ternary structure in an ultra-microscopical dispersion, accounting for the high mechanical properties of the alloy. In fields lower in copper, the ageing effect is produced by the precipitation of  $Mg_2Si$ , while in fields much higher in copper, ageing should be supplemented by a suitable tempering which yields an additional improvement of mechanical properties.

### THE ALUMINUM-NICKEL-COPPER SYSTEM

The aluminum rich alloys of this system are particularly interesting because they form the basis of the "Y" alloys developed in Great Britain. They were investigated by Haughton and Miss Bingham (J. Inst. Met., 1923, vol. 29, p. 71). The present author had drawn the *structural* diagram for two different temperatures from the vertical cross-sectional diagrams of the constitutional prism, as shown by the British authors (Fig. 68). This series includes no homogenous fields of the alpha constituent because the compound  $Al_3Ni$  is not at all soluble in solid aluminum. Omitting from further discussion the variation of the boundaries of different fields on cooling, we will mention the fact that if copper does not exceed 0.8%, the structure remains binary up to at least 10% nickel and consists of alpha (solid solution of copper in aluminum) +  $Al_3Ni$ . With higher amounts of copper and comparatively low content of nickel, the structure is ternary and consists of alpha +  $CuAl_2$  + a ternary compound  $Cu_3NiAl_7$ . The amount of this ternary compound increases with the drop in temperature and with the increase in nickel, until at a composition of 4% copper and 1.5 nickel we have no more plain  $CuAl_2$ , the field showing a binary structure in which alpha is reinforced by the ternary compound. The latter may actually be a ternary compound but it may also represent a mutual solid solution of the two aluminides; in the latter case it can be

understood why it might have much better mechanical strength, less brittleness, and greater hardness than the pure aluminides possess, which would account for the particular strength of the alloy "Y."

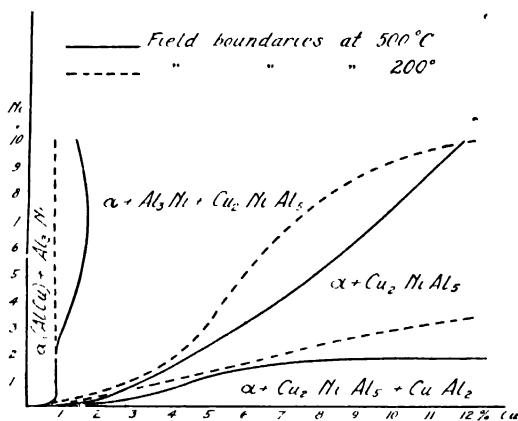


FIG 68. Partial diagram of the Al-Ni-Cu series according to data by Bingham & Houghton (J. I. M., 1923, v. 20, p. 71)

Of course there is not much in this diagram that would indicate a possibility of improving the properties of these alloys by heat treatment, and Rosenhain, who developed these alloys, used substantial amounts of magnesium in connection with the invariably present silicon to make the alloy actually amenable to heat treatment.

### ALUMINUM-MAGNESIUM-ZINC SYSTEM

This ternary system was investigated by the Germans, Sander and Meister. Their investigation was not so elaborate as those of Hanson and Miss Gayler in other ternary alloys, and our Fig. 69, therefore, represents the constitutional diagram only in a schematic way. The dotted line marked 450 shows the limits of saturation of aluminum with both zinc and magnesium. Another dotted line crossing it represents the cross-section along the pseudo-binary system, aluminum +

$\text{MgZn}_2$ , which will be present in the alloys as soon as they contain enough magnesium and zinc. The extreme (dotted) straight lines are the boundaries of the binary fields, one containing  $\alpha + \text{Al}_3\text{Mg}_2$  and another  $\alpha +$  a solid solution of aluminum in zinc, while the major part of the field is occupied by two ternary areas containing  $\alpha + \text{MgZn}_2 + \text{Al}_3\text{Mg}_2$  and  $\alpha + \text{MgZn}_2 + \text{zinc}$ , respectively. The full lines represent the boundaries of the same fields at a temperature of  $150^\circ$ , below which practically no changes may be considered to occur. The German investigators consider 8% Zn

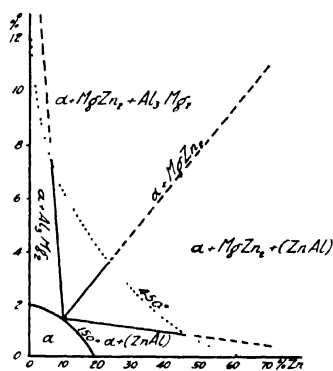


FIG. 60. Partial diagram of Al-MgZn system.

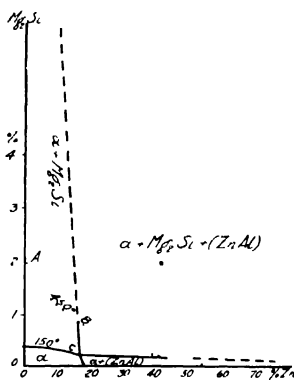


FIG. 70 Partial diagram of the Al-Zn-Mg<sub>2</sub>Si system

as the saturation limit for the solid solution  $\alpha$  at normal temperature. We presume, however, that the British and Japanese data agree more closely with the facts in this particular case.

This system also suggests a theoretical possibility of improving the properties by heat-treatment, due to the drop in saturation during slow cooling and to the mutual influence of magnesium and zinc upon their solubility in solid aluminum. However, the part of the diagram rich in zinc represents alloys which age quickly but do not acquire any particularly desirable properties. Alloys lower in zinc, located at the left and above the line  $\alpha + \text{MgZn}_2$ , are amenable to heat treatment with quite positive results, although the resulting alloys are too sensitive to corrosion to be of much use.



Another system containing magnesium and zinc is pseudo-ternary, because magnesium combines with silicon, yielding actually  $\text{Al} + \text{Mg}_2\text{Si} + \text{Zn}$  (Fig. 70). The conditions in this diagram above  $450^\circ$  (dotted lines) and at about  $150^\circ$  (full lines) are easy to understand. The alloys at the left of the line ABC are also amenable to heat treatment. They actually constitute the basis of a number of alloys studied by the British Light Alloys Committee with the purpose of obtaining compositions as useful as duraluminum with some specially attractive properties. We know, however, that such alloys never became commercially important. The latter is due to the low chemical resistance of the 25% zinc alloy to the action of sea water and to atmospheric corrosion in general. The addition of magnesium only accelerates the chemical action and, therefore, the alloy "E" developed by the National Physical Institute of Great Britain had to be abandoned in spite of its rather high mechanical strength.

#### IMPORTANT TERNARY SYSTEMS STILL AWAITING A CAREFUL EXAMINATION

The aluminum industry of the present day still uses a number of compositions, which were developed by the "cut and try" method.

Nothing would be said against the use of this method, besides its wastefulness, provided it was resorted to in a systematic way.

This, however, is not the fact in the majority of cases. An individual melter simply makes a mixture by rule of thumb and once having made it he "sticks to his guns."

Much waste, illogical, and unnecessary experimenting could be avoided if a certain number of ternary alloy systems were studied more thoroughly. Among such systems awaiting careful examination we may list the following:

1. The Al-Cu-Si systems up to 12% Cu and 13% Si. The problems which must be solved in this field are:

1. The constitutional diagram.

2. The possibility of the formation of a copper silicide or a complex Al-Si-Ca compound.

3. Properties of the cast alloys.

4. Properties of the wrought alloys.

5. Influence of heat treatment in both cases.

6. Effects of a treatment with sodium.

II. The Al-Zn-Si system up to 25% Zn and 13% Si. The same six problems above mentioned must be solved in this case. Besides, there remains an extra problem, namely:

7. The possibility of obtaining a fine eutectic consisting of grainlets of silicon in a ground mass of a strong Al-Zn solid solution.

III. The Al-Fe-Si system. A certain amount of work has already been done on the structural relationships in this case. There remain, however, to be solved the following problems:

1. The actual nature of the "X" constituent.

2. The actual nature of the "Chinese scripts."

3. Their influence upon the mechanical properties of the cast alloys.

IV. The Al-Cu-Mn system up to, say, 12% Cu and 5% Mn. Besides questions 1, 3, 4, 5 we shall have in this case:

2. The formation of double aluminides of copper and manganese.

V-VIII. Systems Al-Fe-Ni

Al-Fe-Co

Al-Fe-Mn

Al-Ni-Mn

Up to 4% of each element.

The special questions arising in these cases are:

1. The formation of double aluminides, its ranges and velocity.

2. Influence of annealing upon the form and distribution of the aluminides.

3. Mechanical influence of the double aluminides as compared to that of the aluminides.

With this information at hand substantial progress in the foundry and rolling mill could be achieved, namely:

1. A definite practice could be adopted in the manufacture of high-grade alumin-silicon castings.

2. The optimum compositions in the manufacture of plain hard alloy sheets and wire (not requiring any heat-treatment) would be better known.

3. The manner in which the additional metals (Ni, Mn, Fe, etc.) influence the properties of duralumin and analogous alloys might have been definitely established.

**PART III**  
**TECHNOLOGY OF ALUMINUM ALLOYS**



## ALUMINUM ALLOYS FOR CASTING

### Historical Review

LONG before aluminum became a market product, certain investigators had foreseen the uses to which this light metal might be adapted and had suggested its use in the form of cast metal. For many years the casting of aluminum did not go beyond the theoretical stage, but as soon as electrolytic production was assured the idea became prominent once more. It was soon discovered that commercially pure aluminum had very inferior properties as to ease of casting, mechanical strength, resistance to wear, and machineability. The alloying of aluminum with other metals, whereby to improve its properties, was begun, but progress was retarded by the undeveloped state of the metallographic science. A general and fairly reasonable impression was that the properties of alloys are defined by arithmetical average of the alloying metals, *i.e.*, that an alloy possesses intermediate specific weights, colors and strengths. For this reason, the first metal applied to aluminum casting was nickel, as presumably able to increase strength and make the alloy more resistant chemically; next iron, as apt to afford an increase in strength; then silver, as likely to make the alloy ductile and give it a better luster; finally magnesium, which would make the alloys lighter and supposedly more free from oxidation. It was soon found, however, that iron gave troubles in foundry work and produced unsound castings without any uniform properties, and that silver does not improve aluminum enough to warrant the use of so expensive a metal. This left nickel and magnesium as the only two metals actually used for aluminum alloy casting in early years, although opinions were expressed and patents issued on the use of high-melting and supposedly far stronger metals like molybdenum, tungsten, etc.

### Magnaliums

The alloys of aluminum and magnesium became known as magnalium, and those of aluminum-nickel (6 to 8% Ni) were called Alloy No. 12 in America. In Europe the strengthening effect of zinc upon aluminum was also discovered quite early, and a number of alloys were suggested for casting work; the best known was alloy 2:1, *i.e.*, containing 33.5% zinc, which was very strong although its specific weight, over 3.5, was comparatively high.

The fields of usefulness for the magnalium alloys and the extent of their industrial importance have always been obscured. The expectations of the early manufacturers of magnalium were so exaggerated that the actual results could not fail to be disappointing. At present, hardly any producers are now making magnalium except on special order. The price of magnesium is much higher than that of many other alloying elements. The mechanical features of the magnaliums can be duplicated with economical amounts of other metals, while the specific weight is not diminished enough to warrant the use of magnesium. Whatever other good properties magnalium may possess have never been clearly stated or proved.

Aluminum-nickel alloys proved to be reliable but far less strong, than was to be expected from the substantial amount of nickel added. The temperatures prescribed for casting were always too high, since the actual melting temperatures were not known and the method of introducing nickel through an auxiliary alloy was not practiced. It did not take the foundryman long to discover that a partial substitution of copper for nickel does not reduce the mechanical strength nor impair the color, makes the alloy cheaper, and permits better working conditions in the foundry. Finally nickel was almost eliminated from foundry work, and an aluminum-copper alloy with 8% copper, previously called "112" to distinguish it from the nickel alloy, became universally established in America under the old name of No. 12. The fields of its application are many and it is the most widely used alloy.

## Alloy No. 12

The hardness of alloy No. 12 being not very high and its wearing properties rather inferior, two other compositions were suggested, one averaging 10.5 and the other 13.0% copper. The 10.5% alloy, with allowance of 1% either way, became established as a reliable alloy for making piston castings; the extra 2.5% of copper proved sufficient to assure good wear, while helping also to give the desired strength at the high temperatures to which gas-engine pistons are subjected. The alloy with 13% copper, although cheap, was found to be too brittle for any part subjected to regular shocks, vibrations, lasting strains, of any kind, although quite satisfactory in regard to its casting and finishing properties; hence it is suitable for parts like manifolds of gas engines, magneto housings, etc. The use of this alloy even for pressure castings, such as bodies of pumps, etc., has been mentioned, but its acknowledged brittleness should preclude the 13% alloy from such fields, especially if the pumps must deliver liquids or gas under pressure.

If we consider the structure of aluminum-copper casting alloys we shall see that under the cooling conditions prevailing in sand molds, they must contain a part of their copper in solid solution, *i.e.*, strengthening the lattice of the aluminum grains, while another and larger part forms grainlets of  $\text{Al}_2\text{Cu}$  which crystallize eutectically and mechanically stiffen the whole structure of the alloy. Now, the relative amounts of copper going into solid solution and into grains of aluminide, as well as the shape and size of the latter, depend largely upon the conditions of cooling, and are rather different in the chill-cast and in the sand-cast products. The shape and particularly the wall thickness of the castings are of highest importance in influencing the distribution of copper in the alloy, and the shape and size of the grains of aluminum and  $\text{Al}_2\text{Cu}$ . The aluminides have a strong crystallizing power, and real eutectics for instance such as can scarcely be resolved into constituents at magnifications of 500 diameters are not readily formed. Even at 40 or 50 diameters we can see the aluminides quite



separated from the remainder of the alloy, and we frequently find the outlines of these grains to be sharp, angular and much larger in one dimension than in the others, which does not add to the strength of the casting as a whole. Accordingly, efforts have to be so directed as to achieve a more uniform distribution of copper between the solid solution and the aluminide, and to refine the grains of the latter while also eliminating their sharp outlines and angles.

The structural shortcomings of the aluminum-copper alloys thus lead to the following mechanical deficiencies:

(1) The elongation which may reach 4% in 2 inches, is too often reduced to 1.5% or less, which explains why no specification requirement can afford to include the higher figure.

(2) Near the solidification point the amount of copper present in copper aluminide is not sufficiently high to prevent completely the internal cracking of castings in thin places and particularly around the cores. The castings are apt to be porous especially in spots where the sharp edges of large sized copper-aluminide particles make defective contact with the ground mass.

(3) Copper-aluminide, if grown large under peculiar conditions of freezing in some parts of the castings, is liable to crumble out during machining or polishing, which makes finishing of the castings difficult.

One of the foremost advantages of the regular 8% composition, as compared with the ones higher in copper, is its ease of machining and polishing, provided the castings are made under the best foundry conditions.

A decrease in the amount of copper added to aluminum avoids certain difficulties and permits higher elongations and better ductility. On the other hand, the amount of aluminide becomes too small and the machining and polishing qualities of the alloy suffer. Shrinkage also is liable to become excessive and the casting of intricate shapes with thin sections and hollow spaces becomes very difficult. Further, the elastic limit and the yieldpoint depend mainly on the amount of copper added:

Another disadvantage of aluminum-copper alloys is the fact that aluminide of copper by itself has a very low melting point; it becomes comparatively weak at temperatures as low as  $150^{\circ}\text{C}$ ., thus injuring the strength of the alloy as a whole.

Many of the disadvantages of aluminum-copper alloys can be overcome by proper melting and casting practice and a proper design of molds; others, however, can not be corrected without the addition of certain other elements.

#### Other Casting Alloys of the Al-Cu Base

Among these additional elements we have to distinguish three classes: The first will increase the stiffness of the lattice of aluminum grains; the second helps in forming certain high-melting aluminides apt to crystallize in fine particles with rounded edges and thus reinforce the action of copper aluminide; the third may form either ternary eutectics or fine suspensions of a soft character, which increase both the ductility and the ease with which the alloy fills a mold and reproduces the outlines of the pattern.

Zinc and magnesium belong to the first class, if their quantities are not excessive; silver, manganese, nickel, cobalt and iron belong to the second; lead and tin to the third. The second class embraces also additions of silicon which will, however, be discussed separately.

Zinc and magnesium are actually used for the strengthening and improving of aluminum-copper alloys. They are not, however, able to afford additional strength at higher temperatures, while by throwing out a larger amount of copper aluminide they make the control of the shape of the  $\text{CuAl}$  more difficult. Silver aluminide,  $\text{Ag}_2\text{Al}$ , melts at quite a high temperature and forms very compact round-edged particles; it would make an excellent strengthener if not so expensive. Manganese and nickel, about equal in price, form aluminides with high melting points and probably also quite isomorphous with copper aluminide, therefore they may be considered the best practical strengtheners of aluminum-copper alloys. The

addition of either one allows the amount of copper to be diminished considerably, with the result that the ductility is increased while the strength remains normal. The action of cobalt has not been studied; it might be serviceable, although its price would be prohibitive in comparison with the slight extra improvement it would probably yield. Finally, chromium might be a very good strengthener, if it were not for the very high melting point of its aluminide and the improbability that the latter would associate with the aluminide of copper. Slight amounts of chromium were found to be of no value in aluminum-copper casting alloys, and the same may be said about other high-melting metals. On the other hand, chromium aluminide should have a comparatively good strengthening influence if another aluminide-forming element were added with it; an auxiliary alloy containing aluminum, nickel, and chromium might help to introduce the latter with good results.

Tin and lead, also cadmium, are supposed to have good effects upon the ductility of cast aluminum, but they undoubtedly cannot contribute to the strength of the cast metal, nor do they decrease the shrinkage of the alloy or its tendency to crack immediately after solidification in the molds; the latter may only become accentuated.

Iron was found to maintain the strength of aluminum-copper alloys at higher temperatures, but special methods have to be adopted for introducing iron into aluminum alloys in such a way as to avoid the formation of hard spots of unmelted aluminum-iron compounds; the usual method is to use auxiliary alloys containing both copper and iron. Iron helps to increase the strength also at normal temperatures, but decreases both ductility and impact resistance disproportionately and shows no improvement of other properties.

Among aluminum-copper alloys improved by the addition of metals of higher melting points, those containing manganese and nickel remain the most conspicuous. It is possible to obtain much better ductility and impact resistance, with an equal strength, in alloys with copper as low as 3% and manganese

or nickel not over 1.5% and 2% respectively. In such alloys, however, practically all the copper will go into solid solution in aluminum while (roughly) only 3 to 5% of aluminides of manganese or nickel remain to reinforce the intergranular boundaries, compared with 9% as in alloy No. 12, or 13% as in the "piston" alloy. This substitution may be advantageous to strength and ductility, but possibly not to machineability and denseness of the casting. The total amount of the aluminide particles which help to refine the grains of aluminum, as an aid to casting, or to interlock them against penetration by liquids and gases might prove insufficient.

As to machineability, aluminum-copper alloys with an addition of zinc or magnesium give the best satisfaction. Additions of magnesium are generally considered as helpful in obtaining very dense castings with a high luster when finished; the latter opinion is correct, but the first is doubtful. At any rate, an addition of magnesium hardens the alloy quite considerably at normal temperatures.

#### Pouring Temperatures, and Foundry Practice

The casting temperatures for aluminum-copper alloys, whether binary or containing additions of other elements, have great influence on the properties of the finished product. For binary alloys, the best temperatures for thick and thin castings respectively are 50 and 75° C. above the complete melting point as given by the constitutional diagram. Alloys to which zinc or magnesium is added require a lower casting temperature, while those containing nickel, manganese, or iron in proportions up to 3% should be cast at 80 to 120° above the melting point of the binary aluminum-copper composition forming their base.

Other foundry conditions favoring the production of satisfactory castings are: the use of comparatively fine sand; ramming the mold as dry as possible; skin drying of molds; use of soft cores, which will collapse under the pressure of the solidifying aluminum instead of causing the latter to crack; the use of chills wherever possible. The aluminum foundries

of France, which serve the automobile and aviation industries, introduce chill castings widely and thoroughly. The chill castings invariably have higher ductility, higher strength, lower shrinkage and greater hardness; they also polish better and are much less porous.

Among the raw materials for the aluminum-copper alloys foundry, the auxiliary alloys containing from 30% to 50% copper are particularly valuable, as they permit the introduction of copper into the final alloy without undue overheating and with no chance of forming hard spots. Such alloys melt so readily that their copper is quickly distributed throughout the whole mass of the aluminum alloy.

#### The Al-Zn-Cu Alloys

The European and most of the English casting practice is still based upon aluminum-zinc alloys. The disadvantages of such compositions are their higher specific weight, their tendency to contract in storage or in work, and sometimes to distort, and in particular their intrinsic weakness at higher temperatures, which limits their fields of usefulness. At present the percentage of zinc introduced into such alloys is rapidly diminishing and the resulting decrease in strength has to be counteracted by the addition of copper and sometimes magnesium. With the addition of copper, an aluminide of the latter is formed which reinforces the metal by its intergranular action. Other additions to aluminum-zinc alloys proved quite worthless and liable to spoil the alloy instead of strengthening it. The lack of constitutional investigations makes it difficult to say in what form nickel, manganese, or iron will be present in an aluminum-high zinc alloy. We can only predict a possible formation of silicides of these metals, since the aluminum will be strongly bound to zinc in the form of a solid solution. It is also possible, at least in high-zinc alloys, that zinc compounds of the high-melting metals might form and be sufficiently brittle to spoil the alloy. In the absence of detailed experimental data, however, we are not entirely free to condemn such additions to aluminum-zinc alloys. The present trend is

to use compositions containing 10 to 15% zinc and 2 to 4% copper.

#### Improving Aluminum Alloy Castings by Heat Treatment

A comparatively recent development of aluminum casting is the use of alloys amenable to heat treatment. Not long ago, alloys containing copper and magnesium besides an additional metal of the high-melting group, *i.e.*, manganese, nickel, iron, cobalt, etc., were considered useful for rolling purposes but never for castings, as their initial mechanical features, particularly machineability and soundness, were inferior and inconstant, while no consistent improvement was obtainable by quenching and ageing. Investigations by American and English experimenters have shown that, under suitable conditions, alloys of this class can be easily heat-treated and thus attain high strength, yield point, and elongation. The necessary conditions for obtaining good results were found to lie, first, in the use of low casting temperatures, almost dry molds and particularly in the use of chills. Next, it was found that alloys to be heat-treated should not be subjected to the action of furnace gases. A neutral atmosphere in the muffle used for heat treatment is desirable, or still better a molten bath of a mixture of sodium and potassium nitrates, which melts at  $260^{\circ}$  and protects the metal from intergranular oxidations along any hair cracks which might be present. Next, a quench in boiling water for some alloys, or in oil for others, followed by a final ageing or tempering between  $100^{\circ}$  and  $200^{\circ}$  C., was found to produce the best and most stable results. Finally, for castings of large size and intricate shape, an anneal at  $500^{\circ}$ , followed by quick air cooling, was found to afford improvement in mechanical features without further heat treatment; quite evidently this improvement is not very great and this method will, therefore, not be resorted to except in some particular cases. Even a plain anneal is found to improve the properties of many castings (particularly their ductility) but is considered too expensive for the majority of cases.

In casting alloys amenable to heat treatment, the amount of

copper generally used never exceeds 5%, the additional elements being either 0.5 to 1.0% manganese, or 1.3 to 2.0% Ni or 1.0 to 1.5% Fe plus 0.2 to 0.5% magnesium. At these compositions, the structure of the heat-treated casting may contain almost all of its copper and magnesium in a state of atomic or at least ultra-microscopic dispersion within the individual grains, the whole intergranular reinforcement being due to the presence of only 1.5 to 5.0% of aluminides. It is, therefore, doubtful whether in such heat-treated castings the improved strength and ductility are supplemented by an interlocking texture and a good machineability. The limitation of copper to 5% (and in most cases 4%) may have good reasons, but they have never been definitely stated. Additional experiments are obviously needed to make this matter clear, and there is reliable information from a French source, that even castings with 14% copper and 1% manganese are amenable to heat-treatment.

The heat-treatment of Al-Cu-Mn-Mg sand castings, Fig. 71, was investigated by L. Jeffries and W. Gibson (Tr. A. M.

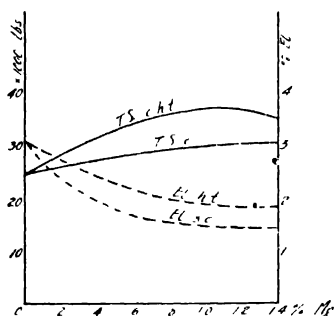


FIG. 71. Influence of quenching and ageing upon the properties of sand-cast alloys containing different amounts of magnesium besides 3% Cu and 1.4% Fe

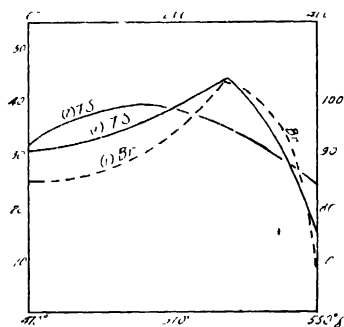


FIG. 72 Influence (1) of the quenching temperature (00 hours) and (2) of the tempering temperature (10 hours) of sand-cast magnalite alloy.

M. E., 1920, vol. 64, p. 270). That of Al-Cu-Ni-Mg sand castings (Magnalite alloy) (Fig. 72), by Lyon and Daniels (J. S. Aut. E-25, 1924, p. 173) and that of the same alloy in

the form of chill castings (British Y alloy) by W. Rosenhain and S. Archbutt (J. Inst. Met., 1922). Finally, that of chill castings of plain Al-Cu alloys by D. Hanson and M. Gayler.<sup>1</sup>

The nomenclature of aluminum alloys for casting purposes is rather confused. We know English alloys, American alloys, German alloys, Navy alloys, S. A. E. alloys, and numerous proprietary alloys. Further, many of them carry identifying numbers. For instance, a 10% zinc alloy is called German No. 7, a 17% zinc alloy is called German No. 20, and an alloy containing 12% zinc and 3% copper is called simply German alloy. Below we give a list of some of these casting alloys and another in which their properties are tabulated. The empty spaces in these tables refer to those properties (as numbered) for which the factors relating to pure aluminum are known, but those relating to the alloys have not been determined.

A number of alloys containing zinc and copper are called "die casting alloys," their compositions, however, being chosen without much critical consideration. It is possible that these alloys were actually found suited for die casting but it is hardly believable that they are the only ones which can be so used. There is an opinion that quite a number of aluminum die castings are made in molds of plaster of Paris which are discarded after the casting; obviously they should not be called die castings.

#### Silumin and Alpac Alloys<sup>2</sup>

One of the more recent innovations in aluminum casting is the introduction of aluminum-silicon alloys, which series is described in a general way in the second part of this book. At first, it seemed impossible to obtain good properties in such castings on account of the crystallization of silicon in large sharp-edged or needle-like grains, not sufficiently bonded with the ground mass and liable to decrease the impact strength very seriously. The methods of treating Al-Si melts as discovered by A. Pacz (NaF or NaOH), by the Aluminum Com-

<sup>1</sup> See Appendix (heat treatment of high copper alloys).

<sup>2</sup> See Appendix (difference between Silumin and Alpac).



pany of America (use of Na), and by the British Aluminum Co. (use of Ca), made it possible to obtain a modified fine granular eutectic, in which form the alloys have exceedingly valuable properties. They are sufficiently strong, almost up to the melting point, and therefore they never crack in the molds. Also they show the least amount of shrinkage, fill the mold well, wear well, and are better than other casting alloys particularly in their resistance to acids, saline solutions, etc. Only sodium hydroxide seems to attack them more strongly than other aluminum alloys.

The properties of aluminum-silicon alloys do not, however, vary continuously with the silicon content. The first 0.7 to 1.7% of silicon form a solid solution with aluminum (particularly in the chill-cast or the annealed state) and thus harden it considerably (up to 35 Brinell). A further addition of silicon does not cause a proportional increase in hardness, which stays between 37 and 43 Brinell (in the sand-cast state) up to almost 10% silicon. It is only the true eutectic composition, not so easily attained and situated somewhere about 14% of silicon in the modified alloy, that gives the metal its strength, hardness, machineability, and maximum corrosion resistance. To secure these features requires, furthermore, a careful treatment, embracing the control of the amount of sodium added, of the time during which it acts upon the melt (10-20 m.) and of the temperature of pouring (650-680 C.).

#### Dix's Alloys

The intergranular strengthening action of the aluminum-silicon eutectic may be combined with that of copper within the grains. In fact alloys containing about 3.5% copper and 4% silicon were found to give reliable and sufficiently strong castings, the strength of which shows only slight deviations in separate test coupons and in specimens cut from the walls of very intricately shaped castings. Other alloys in the aluminum-copper-silicon series might give still better properties. In particular, an alloy containing 6% silicon and 4% copper was found to have high mechanical strength and sufficient elonga-

tion at normal temperatures, and to maintain a constant strength up to 150° C. We venture the opinion that an alloy with 11% silicon and 4% copper if treated by the modifying process, will possess desirable properties and be amenable to improvement either by a simple anneal followed by air cooling or by some more elaborate heat treatment.

It might be profitable to combine the action of silicon in the intergranular spaces with the action of zinc in the crystal-line lattice of the aluminum grains. There is an opinion, probably not quite correct, that alloys of this kind have very inferior properties, and some manufacturers will say bluntly that zinc and silicon "do not go together." At any rate, no information concerning experiments of this kind has ever been published and this question is open to detailed investigation.

#### Difficulties in Aluminum Alloy Casting

In conclusion, let us examine the difficulties in the casting of aluminum alloys and the methods by which they can be overcome.

The first drawback of pure aluminum is that it is rather apt to form large grains, the bonds between which, immediately after forming, are very weak; this makes it quite difficult to obtain sound castings. The introduction of additional elements has the very important purpose of counteracting this difficulty; the more of the additional element, and the more of aluminide or other hard substance that can be formed during freezing, the smaller the grains of aluminum and the more reinforced are their boundaries. A very important prerequisite, however, is that the additional element or its aluminide shall not crystallize first, or at least shall not form large crystals but be distributed in fine grainlets through the whole mass of the casting. This requires the use only of such elements as can be added in fairly large proportions without bringing the whole composition beyond the eutectic point. Accordingly, only small additions of manganese and still smaller additions of chromium or iron are admissible, while nickel can be added up to say 4%, silicon and copper up to 13%, and silver in much larger amounts.

The refinement of the aluminum grains, produced by alloying, causes an increase in the yield point and a decrease in the ductility of the small crystals. The decrease in ductility is accentuated by any deforming action applied, whence cold-working results in a breaking down of the grainlets of the reinforcing aluminides, and leads, in a manner not completely understood, to destruction of the whole casting. This compels us to restrict the amount of the additional metal quite narrowly, or to find a way by which the grainlets may be made so small as to become practically non-brittle. So long as the grainlets of the addition metal or of the formed aluminide are sharp and angular and have varying thicknesses at different places, the alloys containing them are exceedingly sensitive to shock. The impact resistance of aluminum alloys is therefore generally so small as to make it unsafe to use castings made of them in any place where localized shocks may occur.

Another shortcoming of pure aluminum is its great shrinkage. However, practically every additional element which forms a solid solution first and an aluminide next reduces the shrinkage continuously and effectively. Copper, zinc, and magnesium decrease the shrinkage most actively and silicon acts in the same directions. Our information on the shrinkage of aluminum alloys is not altogether complete, but the known values are compiled in the table below.

SHRINKAGE OF ALUMINUM ALLOYS

<i>Composition</i>	<i>Shrinkage</i>	
	<i>Sand cast</i>	<i>Chill cast</i>
8% Cu (Alloy No. 12)	1 41%	1 34%
11% Cu (Piston alloy)	1 38	1 21
14% Cu (Manifold Alloy)	1 33	1 20
8% Cu + 2% Fe	1 44	1 29
8% Cu + 4% Fe		1 21
8% Cu + 5% Mg		1 27
8% Cu + 2% Mg		1 08
8% Cu + 2% Mn	1 40	1 40
8% Cu + 2% Ni	1 42	1 25
8% Cu + 2% Si	1 27	1 17
8% Cu + 2% Sn	1 40	1 26
8% Cu + 2% Zn	1 38	1 29
14% Cu + 1% Ni		1 24

Besides the two mentioned intrinsic weaknesses of aluminum, two other troubles are encountered in the casting industry.

#### Films of Aluminum Oxide

First, the making of an aluminum alloy for casting necessitates a considerable amount of stirring, which is done with iron or graphite bars. Stirring not only breaks the film of oxide floating on the surface of the metal, thus exposing it to continuous oxidation, but also admits air well into the interior of the molten mass. The aluminum oxide thus introduced in the metal does not readily separate by standing, owing to the small difference in the specific gravities involved. Then, during the pouring, the stream of molten alloy has abundant opportunity to become still more oxidized, and the oxide is drawn into the mold. The latter, if made in sand, generally holds considerable moisture as well as air, both of which react with aluminum and increase the amount of oxide in the finished casting. Thus the problem of eliminating oxide is almost hopeless so long as the present customs of pouring and of making the mold are retained.

Many remedies have been suggested for the elimination of aluminum oxide. One employs small pieces (nut size) of zinc chloride thrown upon the surface of the molten metal before pouring, the amount of chloride not exceeding 1, 8% of the total weight of metal. Since zinc chloride evaporates violently at 730° C., the metal in a crucible has hardly any chance to remain in contact with it. It is doubtful, furthermore, whether zinc chloride reacts to any extent with aluminum oxide, and finally the surface layer is only a small part of the whole problem relating to oxide.

Another method consists in dissolving aluminum oxide by stirring in sodium fluoride or a mixture of the latter with potassium fluoride or calcium fluoride. Pure sodium fluoride melts at so high a temperature that unless the metal is overheated no actual dissolution of aluminum oxide can take place; hence a mixture of fluorides is necessary. Very thorough stirring of the molten fluoride of course is necessary to bring

it in contact with the unevenly distributed aluminum oxide. Even if the latter is accomplished, the likelihood remains that the drops of sodium fluoride, made more viscous by the dissolved alumina, will themselves be slow in rising to the surface and remain in substantial amounts within the molten metal, to form holes in the finished casting. It is safe to say, therefore, that there is no other way to eliminate aluminum oxide than to work under such conditions that the surface film of oxide has no chance to be stirred into the metal.

#### Hard Spots

A second frequent difficulty encountered in the casting of aluminum is its tendency to develop hard spots due either to inclusions of undissolved iron or to primarily precipitated large needles of iron aluminide, which is unavoidably formed when aluminum is melted in cast-iron pots. Nevertheless, the amount of aluminide immediately dissolved is neither large nor of much consequence; in some cases it may even be useful. As soon, however, as the inside of an iron crucible becomes covered with a substantial crust of iron aluminide, the latter crumbles out and remains in the aluminum in the form of mechanical inclusions. These are hard, spoil the tools, and completely ruin the appearance of the finished casting.

The necessity for adding at least a part of the scrap from previous castings (gates, risers, etc.) is a source of an almost unavoidable admixture of fine particles of iron coming from the tools used in roughing and finishing the castings. These particles of iron are generally covered with a film of oxide and therefore do not react with aluminum but remain as such in the finished casting. The hard spots due to iron and iron aluminide are very difficult to eliminate in foundries doing a general business, and necessitate the use of graphite pots, separating magnets, and other devices which add to the expense of casting.

#### Improved Foundry Methods

Two other difficulties which aluminum foundries have to meet are porosity of the castings and their inferior machine-

ability. Porosity is due to aluminum oxide, to various mechanical inclusions, and to the uneven distribution of copper aluminides. A reduction in the amount of copper aluminides is frequently accomplished by substituting the aluminides of manganese or nickel; in fact, castings of the same strength and much better ductility are now being made in the "Navy Metal," containing 2% copper and 1% manganese instead of 8% copper. This substitution, however, must result in an inferior machineability, since this depends on the amount of the eutectic constituent in the alloy.

A number of difficulties in the aluminum foundry are being avoided by the use of certain new alloys, such as alpax (or silumin) a modified eutectic alloy of aluminum with silicon, previously mentioned. This is almost the only alloy with a true eutectic structure which can be made so fine as not to include grainlets larger than 0.001 mm. for aluminum and 0.0003 mm. for silicon. However, the preparation of this alloy is somewhat delicate and requires most careful attention to the temperatures of the furnace, of the modifying treating, etc. Too long an interval of time in passing from the temperature of treatment to the temperature of pouring may vitiate the entire modifying action. The presence of extra sodium or sodium fluoride in the alloy may also prove detrimental. Furthermore, in the modifying treatment the composition must be close to 13.8% silicon, as required to form the eutectic; a reduction of 2% in silicon will leave large patches of primary aluminum, and the mechanical properties will be impaired. Every property of this alloy, including strength, hardness, chemical resistivity, and machineability, is intimately related to the eutectic composition.

A possible means for overcoming some of the defects of regular aluminum alloys lies in the use of a ternary alloy containing enough copper to strengthen the aluminum by forming a solid solution, and exactly enough silicon to form a strong eutectical network. Experiments are being made in this direction, but the most suitable composition has not yet been found.

Finally, any of the alloys, alpax, alloy No. 12, Navy metal,

etc., can be made to give reliable castings with excellent machineability, absence of porosity, etc., by a complete change in the procedure of melting, pouring, and molding. The greatest improvement is afforded by the application of graphite or metal chills wherever possible, in order to produce refined grains in both the aluminum and the strengthening constituents. Arrangements for melting in open-hearth furnaces (preferably electrically heated) and complete changes in methods of pouring (for example, admitting the molten metal to the mold through closed pipes under the influence of suction) must certainly yield improvements as to strength of metal, absence of oxide, minimum porosity, and other features of casting practice.

A far-reaching improvement in the methods of aluminum alloy casting was lately developed by Archbutt (*J. I. Met.*, 1925, v. 33, p. 227), at least on the experimental scale. His method consists in allowing the thoroughly stirred melt to freeze in the crucible and immediately remelting it again. Undisturbed freezing in the crucible helps to remove dissolved gases and to bring oxides to the surface. In consequence very sound and dense castings are obtained even in said moulds. The author tried this method out and found it excellent for aluminum-copper alloys with additions of Mn, Ni, Fe, etc. It has had less influence in the case of Alpac castings.





TABLE II.  
LIST OF USED OR SUGGESTED ALUMINUM ALLOYS FOR CASTING WORK

No.	Name or Trademark	Composition	Remarks
1	American No. 12	8% Cu	Varies from 7 to 9% Cu
2	L-8 (British)	12% Cu	Identical to American No. 12
3	Am. piston alloy	0-11% Cu	Averages 10 5% Cu
4	American Manifold Alloy	11-14% Cu	Averages 12 5% Cu
5	14:1 (British)	14% Cu 1% Mn.	Pract. identical to Amer. alloy for manifolds
6	"Magnalium"	5-10% Mg	Actual composition unknown
7	German "Al 20"	17% Zn	
8	Alpax or Silumin	10% Si	
9	No. 31 (also "German Alloy")	12-15% silicon treated with NaFl, NaHO, Na O <sub>2</sub> Ca	Used for the last 4 years and gaining grounds
10	L-5 (British)	12-15% Zn + 3-4% Cu	Identical with the "German Alloy"
11	British "A"	13% Zn, 3% Cu	Amenable to heat treatment
12	Navy N	3% Cu, 20% Zn	Developed by the American Navy
13	Navy	Higher limits 6% Cu, 3% Mn	T. S. 18,000 lbs. El. 8% sand cast
14	Magnalite	Regular 2% Cu, 1% Mn	
15	British Y	6% Si, 4% Cu	
16	Diecasting	4% Cu, 1 5% Ni, 1 5% Mg, 6% Fe	Highly amenable to heat treatment
17	"Diecasting"	4% Cu, 2 5% Ni, 1 0% Mg	" " " "
18		14% Zn, 3 5% Cu, 7% Fe	" " " "
19		12-14% Cu, 2-3 5% Zn, 7% Fe	" " " "

16 British 2:1

"Magnalium X"

German "119"

" "Al 7"

S.A.E. No. 35

Diecasting

"Al. Cast. Co."

Aluminite

Lynite 146

" 195

Mac Adamite

McLure

Maluminum

T Metal

Verilite

Alzene

Acieral

Aero

33 4% Zn

3 5% Cu + 4 0% Si

2 0 Cu, 2 0 Mg, 1 0 Ni

Composition not stated

10% Zn

4 5-6 5 Si

12% Cu, 1 6% Zn

3% Cu, 7-8% Zn, 1 0-1.3% Fe

2% Mg

3% Cu, 23% Zn

8 5% Cu, 2% Mg, 1 2% Fe

4 6% Cu, 1% Mg, 6% Fe, 05% Si

12-18% Zn, 3% Cu, 2% Mg

8% Cu, 2% Mn, .9% Fe

6 5% Cu, 5% Zn, 1 4% Fe

3 8% Mg

2 5% Cu, 3% Mn, 7% Fe

Very high in Zinc

6 4% Cu, 4% Zn, 9% Ni

4% Cu, 28% Zn

P. L. 5200; U.S. 19,000; El. 1.4%

Amenable to heat treatment

T. S. 16,000; El. 3 5% sand cast

Self improvable in storing

Identical with the British "A"

Amenable to heat treatment

(Pr. Lm. 6,000; U. S. 26,000; El.

0 5%

(Pr. Lm. 8,500; U. S. 31,000; El.

2.5%

Y.P. 18,000; T. S. 31,000

Y.P. 15,700; T. S. 19,600; El. 3 0%

Y.P. 13,000; T. S. 17,000; El. 1.5%

T. S. 16,000; El. 3%

T. S. 16,000; El. 4%

Seemingly identical to the "2.1"

Prop. lim. 6,000; T. S. 22,000; El.

2% sand cast

T. S. 24,500; El. 1 0% sand cast

TABLE III.  
PROPERTIES OF ALUMINUM CASTING ALLOYS IN REGULAR USE

No. of Alloy	1	2	3	4	5	6
	<i>Alloy No. 12 U.S.</i>					
No. of Property	8% Cu	10% Cu	12-13% Cu	14% Cu and 14 Cu, 1 Mn.	Magnalium 5-6% Mg	German No. 20 17% Zn
1	2 89				2 63	$\frac{2\ 93}{S.C.}$
2	23 1-24 6					26 0
6		$630^{\circ} - 540^{\circ}$	$618^{\circ} - 540^{\circ}$	$620^{\circ} - 548^{\circ}$	$630^{\circ} - 575^{\circ}$	$630^{\circ} - 575^{\circ}$
10	0 348		3 80	0 260		.308
14		$\frac{3\ 65}{C.A.}, \frac{4\ 15}{C.O.}$		$\frac{3\ 85}{C.A.}, \frac{4\ 54}{C.O.}$	5 2	$\frac{4\ 7}{15^{\circ}}, \frac{5\ 9}{100^{\circ}}$
23						
28	$\frac{23\ 000}{Ch.C.}$	$\frac{27\ 500}{C.C.}$		$\frac{20\ 500}{C.C.}$	$\frac{20\ 000 - 23\ 000}{S.C.}$	$\frac{24\ 000}{S.C.}$
	$\frac{20\ 000}{S.C. 670^{\circ}}$	$\frac{21\ 500}{S.C. 650^{\circ}}$		$\frac{22\ 000}{C.C. \& 200^{\circ}}$		$\frac{10\ 000, 14\ 000}{150^{\circ}, 200^{\circ}}$
	$\frac{17\ 000}{S.C. 830^{\circ}}$					$\frac{7\ 000}{300^{\circ}}$
	$\frac{17\ 600, 13\ 300}{150^{\circ}, 200^{\circ}}$					
	$\frac{2\ 000}{300^{\circ}}$					

	$\frac{14500}{\text{s.c. crankcase}}$						
29	$\frac{14500}{\text{s.c.}}; \frac{16000}{\text{c.c.}}$	15000					$\frac{15000}{\text{c.c.}}; \frac{22000}{\text{s.c.}}$
30	$\frac{7500}{\text{s.c.}}$						$\frac{5000}{\text{s.c.}}$
31	$\frac{35}{\text{c.c.}}; \frac{15}{\text{s.c.}}$	10-35			$\frac{1-5}{\text{s.c.}}; \frac{5}{\text{c.c.}}$		$\frac{2-40}{\text{s.c.}}$
32	$\frac{70}{\text{c.c.}}; \frac{15}{\text{s.c.}}$						$\frac{70}{\text{c.c.}}; \frac{25}{\text{s.c.}}$
33	$\frac{61}{15}; \frac{44}{200}$	66 s.c.	$\frac{68}{\text{s.c.}}$	$\frac{70}{\text{s.c.}}$	63		$\frac{77}{\text{s.c.}}$
	$\frac{27}{300}; \frac{12}{400}$						
34							
35					11		10
36							
40	$\frac{65}{\text{s.c.}}; \frac{100}{\text{c.c.}}$						
41	$N = \frac{(6800)^{.750}}{S}$						
42	$\frac{660}{\text{c.c.}}; \frac{690}{\text{s.c.}}$	$\frac{680}{\text{c.c.}}; \frac{720}{\text{s.c.}}$	$\frac{670}{\text{c.c.}}; \frac{700}{\text{s.c.}}$	$\frac{670}{\text{c.c.}}; \frac{700}{\text{s.c.}}$	$\frac{670}{\text{c.c.}}; \frac{700}{\text{s.c.}}$		
51	$\frac{.0134}{\text{c.c.}}; \frac{.0141}{\text{s.c.}}$	$\frac{.0121}{\text{c.c.}}; \frac{.0138}{\text{s.c.}}$	$\frac{.0120}{\text{c.c.}}; \frac{.0133}{\text{s.c.}}$				$\frac{.0142}{\text{c.c.}}; \frac{.0155}{\text{s.c.}}$

## CASTING ALLOYS

No. of Alloy	7	8	9	10	11
No. of Properly		<i>Alpac or Silumin.</i>	<i>Alloy No. 31</i>	<i>British No. "A"</i>	
	10% Si	13% Si	3-4% Cu 12-15% Zn	3% Cu, 25% Zn	20 Cu; 10 Mn
1	2 65	2 50			2 85
2		22.2	18.4		
6	595 - 578°	68° - 5 $\frac{78}{78}$	645 - 600°	625 - 560°	650 - 640°
10	386	400	335		
14	3 62	3 75			
23					
28	31500 highest	30000 sep. test piece	23000 s.c. 700°	40000 s.c.	21000 s.c. 700°
	26000 average	19800 part of a casting	37000 ac. 500°		
	24000; 21700 150°; 200°				
	12600 300°				
29	15000 c.c.	19000 c.c.	3300 s.c. 700°		

30	8000 c.c.	40000 s.c.	12500 c.c.	5000 s.c.	$\frac{6000}{ac. 500^\circ}$		
31	3.0		2.5		$\frac{2.5}{s.c.}, \frac{5.5}{ac. 500^\circ}$	$\frac{0}{s.c.}$	$\frac{7.0}{s.c. 700^\circ}$
	90						
	150° - 300°						
32					$\frac{10.0}{ac. 500^\circ}$	$\frac{0}{s.c.}$	$\frac{8.5}{s.c. 700^\circ}$
33	$\frac{41}{s.c.}$		$\frac{53}{s.c.}$		$\frac{62}{15^\circ}, \frac{35}{200^\circ}, \frac{16}{300^\circ} c.c.$		
	$\frac{40}{c.c.}$		$\frac{63}{c.c.}$		$\frac{79}{15^\circ}, \frac{36}{200^\circ}, \frac{15}{300^\circ} s.c.$		
34							
35	$\frac{11 (c.c.)}{un. f.}$		$\frac{15 (c.c.)}{un. h.}$		$\frac{20}{s.c. 700^\circ}$		
39	$\frac{50 lb. ft.}{s.c.}$		$\frac{7 lb. ft.}{s.c.}$				
40	3.5		2.5		$\frac{3.3}{s.c.}, \frac{4.6}{c.c.}$		
41					$N = \left( \frac{9100}{S} \right)^{1/30}$		$N = \left( \frac{65000}{S} \right)^{1/20}$
42	650 - 685°		630 - 670°		$\frac{700}{s.c.} - \frac{710}{c.c.}$	$\frac{675}{s.c.} - \frac{710}{c.c.}$	$\frac{700}{s.c.} - \frac{730}{c.c.}$
51	.0128		0.111				

## CASTING ALLOYS USED

No. of Alloy	12	13	14	15	16
No. of Data	"Y" alloy				
1	4Cu. 6Si	4Cu. 2Ni. 1 5Mg	3 5Cu. 14Zn. 7Fe	13Cu. 2 5Zn. 7Fe	British 2 1 33 4 5Zn
2	2 00	2 80			3 65
6	23 2				
10	630° - 590°	650° - 640°			600° - 510°
14		280			
23					5 2
28	23500 (s.c. 710°)	31600 ; 28200 c.c. 650° ; c.c. 750°	25200 (c. 700°)	30000 c. 640° ag. 2m.	40000 c.
	23800 ; 13600 150° ; 320°	s.c. 700° ; s.c. 750° 27000 ; 23800			
		22400 ; 19600 250° ; 300°			
		10200 350°			
		45000 - 51000 s.c. heat treated			
29	13000	14000 s.c. 700°	19000	23100	32000

30	$\frac{8000}{\text{s.c.}}$				
31	$\frac{15}{(\text{c. } 710^\circ)}$	$\frac{15}{\text{c. } 700^\circ}$	$\frac{60}{\text{c.h.t.}}$	40	20
	$\frac{25}{150^\circ}$ $\frac{53}{320^\circ}$				
32					
33	$\frac{58}{\text{s.c.}}$	$\frac{76}{15^\circ}$ $\frac{68}{200^\circ}$ $\frac{53}{300^\circ}$			85
		$\frac{71}{15^\circ}$ $\frac{61}{200^\circ}$ $\frac{46}{300^\circ}$ s.c.			
34					
35	$\frac{13}{\text{s.c.}}$	$\frac{18}{\text{s.c. un. h.}}$			17
39					$\frac{200}{\text{c.c.}}$ $\frac{350}{\text{s.c.}}$
40	$\frac{275 \text{ lb. ft.}}{\text{s.c. } 710^\circ}$				
41		$N = \left( \frac{75000}{S} \right)^{.08} \text{ h.t.}$			
42	$680^\circ - 720^\circ$	$725^\circ - 750^\circ$			$640^\circ - 670^\circ$
51	0131				.0128 - .0132



## ALUMINUM ALLOYS USED FOR WROUGHT SHAPES

Aluminum, whether pure or commercial, is generally used in the form of sheets, rods, and wire of various sizes. Where softness and ability to stand a large amount of shaping by pressure are required, this non-alloyed aluminum is the best. However, there are many instances in engineering lines, and also in the manufacture of utensils for the home and industry, where stiffness is of the highest importance, and this cannot be obtained unless aluminum is alloyed with some element which is stiffer and tougher than itself.

• As we have seen in part 2, describing different binary and ternary systems, aluminum can easily be alloyed with at least 5% of any of the more common metals and these alloys can be hot-rolled and given a cold finish. On account of the low specific gravity of aluminum, the heavier aluminides formed by the additional metals occupy a comparatively small volume. These aluminides do not form continuous chains, nor are they so abundant as to form large segregations of a brittle eutectic. Hence, aluminum when hot easily flows around the grains of the aluminide without breaking them and without having its own grains torn apart. When cold, however, aluminum in an alloy does not have so marked an ability to flow, whence, aluminum alloys are not suited for extensive cold work; very small percentage of cold rolling or drawing suffices to make such alloys thoroughly hard, while excessive cold work produces internal cracks.

The annealed alloys of aluminum with small quantities of other metals show a lasting increase in hardness, a very pronounced rise in elastic limit and yieldpoint, and a drop in elongation.

Another property of aluminum, its general inability to form rich solid solutions with other elements at normal temperatures (with the exception of zinc) resulting in only a very slight deformation of lattice in such solid solutions, makes aluminum comparatively insensitive to the influence of other metals upon its electrical conductivity. Small amounts of metals like

chromium, nickel, vanadium, and cobalt therefore suffice to harden aluminum considerably by intergranular reinforcement and by grain refinement without greatly lowering its conductivity. Aluminum alloys of this kind may be found exceptionally good for electric cables.

The use of manganese in amounts up to 1.5% for making hard grades of aluminum sheet and wire, is particularly common in the United States and Great Britain. In the mentioned amount manganese affects in the least degree the high resistivity of pure aluminum to fresh and salt-water corrosion.

In spite of the high workability of practically all aluminum alloys not containing excessive amounts of additional metals, only few combinations are regularly employed. One of the best is an alloy of aluminum with silver up to 5%; this has a high silvery luster, is very stable under atmospheric influences, and has excellent mechanical properties; the combination, of course, is expensive.

The aluminum alloys by far the most widely used for rolling work are those containing copper in amounts up to 6%, the average being no higher than 4%. This particular series of alloys rolls exceptionally well even in the cold state, and produces reliable sheet and rod metal. Furthermore, the addition of copper brings aluminum into the field of heat-treatable alloys, where the largest proportion of aluminum-copper alloy is used.

Aluminum-nickel alloys, containing up to 2% nickel, form a widely used hard aluminum composition in Great Britain and Japan.

Wrought aluminum-zinc alloys are at least as easy to make as aluminum-copper. The product, however, looks a little grayish and is not altogether suitable under various conditions of aqueous and atmospheric corrosion.

Aluminum-magnesium alloys are not widely used in the rolled state — far less than alloys containing nickel and manganese. Quite a large proportion of the latter alloys have ternary compositions, containing both copper and zinc, copper and nickel, or copper and manganese.

Rods, tubes and even more intricate shapes are now being made from aluminum or its alloys by the extrusion method. Extrusion seems to refine the alloys to a marked extent, while greatly increasing their strength and ductility provided the billets are made up to special requirements. Ternary alloys containing small amounts of copper with zinc, or zinc with magnesium, sometimes also with additions of tin, are being used for extrusion. Of particular interest are the alloys high in magnesium (up to 12%) which give extruded rods and shapes with exceedingly high strength and comparatively high ductility. The latter shows a minimum at about 5% magnesium, while the alloy with 10% magnesium is at a maximum of both strength and ductility. These alloys, after being extruded, may still be subjected to a slight amount of cold work leading to an additional increase in strength. They may also be made ternary by the addition of small amounts of silicon (2%), in which case strengths of 67,000 pounds with 2% elongation can be easily obtained without heat treatment. An annealed alloy of this kind has up to 45,000 pounds strength with 10% elongation.

The list of aluminum alloys used in rolling work is much shorter than that in casting; the following includes alloys used either in the normal or in the heat-treated state:



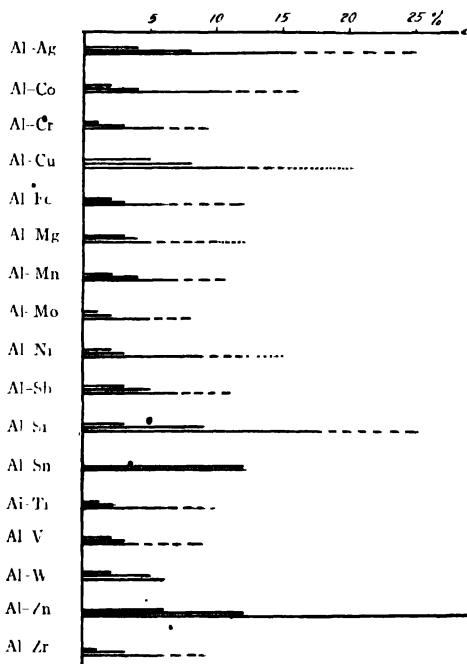
TABLE IV.  
ALUMINUM ALLOYS USED FOR ROLLING AND EXTRUSION

No.	Trade Mark	Composition	Properties	Remarks
1	2 S	1.00% impurities	T.S. = 13,500-35,000; El-n = 30-2%	Regular commercial aluminum
2	3 S	1.25% Mn	" " 17,000 45,000 " " 25 2%	Hard aluminum (Al. Co. of America)
3	Navy metal	2.0-3.0% Cu; 1.0-2.0% Mn		
4	#4	4.0% Cu		
5	Magnalium "Z"	3% Sn; 1.5% Al <sub>2</sub> O <sub>3</sub>	" " 22,000-50,000; Y.P. " 8,000-38,000.	European hard aluminum Extrusion Alloy
6	Magnalium	5-10% Mg		
7	Aero	2.5% Mg	T.S. " 65,000; " " 40,000; " " 40,000;	Extrusion work
8	Aludur 333D	0.8% Mg; 0.7% Si	" " 60,000; Br. " 60 110	European self-ageing alloy
9	Aludur 570J	?	T.S. " 16,000-35,000-48,000; Y.P. " 5,000-17,000-35,000;	
10	Magnalium	2.0% Mg; 20% Si	" " 22-25-15% Al. Co. of America	
11	51 S	1.5 Mg + 1.0 Si	Br. " 28-62-92	Original alloys
12	Duralumin	2-5% Cu; 0.5-0.8% Mg; 1.0% Mn; no other additions		

13	25 S	3-5% Cu + 1-2% Mn +; 1% Si	T.S. " 30,000-49,000- 59,000; Y.P. " 8,000-21,000-	El-n " 17-17-21% Al. Co. of America	
14	17 S	3-5% Cu + 0.7% Mg +; 1.0% Mn	T.S. " 30,000-59,000; Y.P. " 8,000-35,000;	Br. " 47-77-110 El-n " 17-22% Al. Co. of America	
15	Acieral	2.3-3.8% Cu; 0.2-0.5% Mg; 1.0-1.5% Mn; 1.5% Fe	T.S. " 30,000-59,000; Y.P. " 8,000-35,000;	Br. " 46-110 French and American Vari- ations	
16	Lautal	3.0% Cu; 3.0% Si	T.S. " 57,000; Y.P. " 42,000;	El-n " 20.0% A new German alloy	
17	Scleron	0.5% Li; 5% Cu + 2 8% other additions	T.S. " 53,000; El Lim 29,000;	El-n " 92 " " "	
18	Ziscon	25% Zn		El-n " 15% " " "	
19	Rivet metal	20% Zn; 3% Cu		Br. " 90-120 Hardly used at present	
20	British A	3% Cu + 20% Zn			
21	"	2 3% Cu; 20.0% Zn; 0.5% Mg; 0.5% Mn			Exprim. Alloy; amenable to heat-treatment
22	"	2.5% Cu; 18.0% Zn; 0.35% Mg; 0.35% Mn	El. Lim. 54,000 Y.P. = 65,000 T.S. = 77,000;	El-n " 19.0% Exprim. Alloy; amenable to heat-treatment	
23	"	4.0% Cu; 2.0% Ni; 0.5% Mg	" " 60,000; Y.P. " 50,000	" " 12.0% Exprim. Alloy; amenable to heat-treatment Rolls with difficulty	

The suitability of aluminum alloys for sheet rolling was studied by Schirmeister (Stahl und Eisen, 1916, vol. 35, p. 648 *et seq.*) for some twenty different series. Mechanical properties of his products in the annealed state are represented in the diagrams attached to the description of the corresponding series, where curves drawn from Schirmeister's data (slightly idealized) are marked r. a. (rolled and annealed). In connection with Schirmeister's results, supplemented by additional information, a diagram is given below showing the workability of different aluminum alloy series.

The heat-treatable wrought aluminum alloys require a more detailed description, which is given in the next chapter.



The workability extent of different binary aluminum alloys.  
 — cold rollable to 50% reduction, - - - cold rollable to 10%, — hot rollable, — — — hot forgeable, . . . extrudable.

## DURALUMIN AND ANALOGOUS ALLOYS

The discovery of duralumin resulted from a year's work by A. Wilm, the latter's work being first published in 1911 (*Metallurgie*, vol. 8, p. 650). Wilm apparently was engaged in studying the properties of aluminum-magnesium alloys and finding nothing of particular advantage, within the simple conditions of the binary series at least, he turned to the investigation of ternary series, that of aluminum-copper-magnesium being quite naturally the first. Here he incidentally discovered that some rolled and annealed alloys, after being quenched at a temperature within the range of  $450^{\circ}$  to  $525^{\circ}$  C., acquired the property of ageing, under which they hardened a great deal, their strength and yield point increased greatly, while their ductility remained unchanged or, in some cases, was even improved. Wilm found that the best alloys contained copper within 3 to 5% and magnesium within 0.5 to 1%. He also discovered that an addition of manganese in amounts not exceeding 0.8% gave increased chemical resistance and a further increase in the strength and hardness of the alloy.

Wilm himself apparently did not attempt to learn the actual causes of the discovered phenomena, but ascribed them to the formation of a saturated solid solution at high temperature and its preservation after quenching, followed by some minor transformations during ageing. After Wilm, many other experimenters occupied themselves with duralumin from the two viewpoints: (1) the mechanism of quenching and ageing; (2) the best methods for obtaining light alloys of high strength with properties easily duplicated in a commercial way. The theory is not yet clear although a large number of scientists have worked on it for the last 12 years in Germany, France, England, and America. The individual viewpoints can be gathered by consulting the following publications:

1. 1919. Merica, Waltenberg and Scott. U. S. Bur. Stds. Sci. Papers 347.
2. 1919. Z. Jeffries. J. Inst. Metals, part 2, p. 329.
3. 1920. W. Fraenkel and R. Song. Z. fur Metallkunde, p. 427.



4. 1921. W. Rosenhain. Engineering, July 29, p. 192.
5. 1921. L. Guillet. C. R., No. 173, p. 979.
6. 1922. D. Hanson and M. Gayler. J. Inst. Metals, part 1, p. 266.
7. 1922. W. Fraenkel. Z. fur Metallkunde, pp. 49 and 111.
8. 1922. S. Konno. Sci. Rep. Toh. Imp. University, vol. 11, No. 4, p. 269.
9. 1923. A. Portevin and H. Chevenard. J. Inst. Metals, vol. 30, p. 329.
10. 1924. A. Portevin and P. LeChatelier. Trans. Am. Soc. Steel Treat., p. 457.

Theoretically, the processes fall into three groups: high-temperature treating, quenching, and ageing. As to the first, there is no doubt that some alloys of aluminum, particularly those containing copper or zinc or magnesium (accompanied by silicon), have a much wider range of solid solubility at higher temperatures for any one of these elements or for a group of them. Hence, it is quite possible to bring into solid solution a comparatively large amount of zinc, or 5% of copper, or about 1.5% of magnesium silicide by a prolonged heat-treatment at a temperature around 500°. In the resulting solid solution the additional metals may be distributed without any particular order, the different new atoms occupying the place generally taken by atoms of aluminum. On the other hand, it is also possible that the stranger atoms may not remain in this state of purely atomic dispersion in the solid solution and in identical relationship to all of the neighboring aluminum atoms, but that some if not all of the stranger atoms may be more intimately connected with particular atoms either aluminum or of the second additional element (for instance, Mg to Si) forming the same compounds as can be observed in annealed aluminum alloys.

The state of saturated solid solution, when attained, may be preserved, at least apparently, at normal temperatures by increasing the rapidity of cooling with the use of some quenching medium. In fact, it requires rather slow cooling, almost unattainable in regular furnace practice, to break down the

solid solution continuously and completely, and a part of the additional element almost always remains in the form of a super-saturated solid solution; wherefore, even a simple cooling in air produces something of a quenching effect. The fully equilibrated state can be obtained by a prolonged heating at a temperature at which the agglomerating effect is strong enough to precipitate the resultant compound completely.

The ageing process is the most difficult to explain. One theory suggests that in the quenched state the additional elements are still dispersed in a purely atomic manner, while in the ageing process they recombine to form molecules of the corresponding compounds, for instance,  $\text{Al}_2\text{Cu}$  for copper, and  $\text{Mg}_2\text{Si}$  for magnesium and silicon. This formation of compounds might aggravate the deformation in the crystalline lattice, making it stiffer and thus producing the increased strength and hardness of the alloy as a whole.

Another theory starts with the idea that quenching leaves the additional elements in the form of loose, free atoms and that during the process of ageing these atoms form compounds which agglomerate in a continuous manner. Agglomeration is supposed to occur with diminishing speed, and to be completed after a definite time for every temperature below the range of complete recrystallization. During this period of ageing or tempering the agglomerated particles become large enough to form "keys," interfering with the slip along the cleavage planes in the apparently homogeneous grains of the quenched solid solution.

The ageing process becomes more rapid with an increase in temperature, and a tempering up to about  $200^\circ\text{C}$ . may be adopted to obtain the final properties of the various alloys in the shortest time. At some temperature, however, agglomeration goes beyond the critical size, from which point the alloy becomes weaker until it reaches the minimum at a temperature at which the fully equilibrated condition can be obtained by a suitably long anneal. This temperature represents also the recrystallization point for the grains of the low-alloyed solid solution, and varies, for different compositions, somewhere between

300° and 370° C. In a fully annealed state the maximum amounts of  $\text{Al}_2\text{Cu}$  and  $\text{Mg}_2\text{Si}$  are precipitated.

No theory of duralumin hardening accounts completely for all the facts. In particular, the most plausible theory of "critical agglomeration" stumbles on the fact that the electric resistance of duralumin increases with ageing instead of diminishing, as it should if a primary solid solution were actually undergoing ultra-microscopical dissociation. Certain other factors in fair agreement with the slip interference theory cannot be reconciled with other theories such as the "intermediate phase" or the formation of compounds within the quenched and aged grains of duralumin.

Two facts are the most difficult of explanation from the viewpoint of the slip interference theory, and they consist in the exactly opposite behavior of duralumin as self-aged and heat-aged. In the first case the electric resistivity increases and so does the corrosion resistance. In the second case both decrease.

The latter phenomena are easy to explain. The presence of copper in solid solution makes aluminum a more noble metal, while the presence of the precipitated particles of  $\text{Al}_2\text{Cu}$  creates potential differences and starts corrosive actions. On the other hand, the atomically dispersed copper (in solid solution) increases the resistivity to the electric current, while the precipitated individual particles of  $\text{CuAl}_2$  are almost harmless.

In the case of self-aged duralumin it is the  $\text{Mg}_2\text{Si}$  compound which precipitates and of course it might have been expected on first thought that the dropping out of two atoms of magnesium and one of silicon from the solid solution in aluminum would tend to decrease the resistivity. In fact, in the English "Aludur" metal or the American alloy "51S," the electric resistivity decreases on ageing.

The entirely unexpected results of duralumin age-hardening can, however, be explained along the following ideas developed by the author.

In the quenched duralumin we have in general 6 atoms of copper to 2 atoms of magnesium and 1 atom of silicon. The

copper atom is heavy; its atomic volume of 7.1 tends to shorten the inter-atomic distances in the aluminum lattice, inasmuch as the latter metal has an atomic volume of 10.0.

Magnesium and silicon with atomic volumina (space occupied by a gramm-atom of the element) of 11.4 and 14.1 respectively, must tend to expand the interatomic distances and therefore they *ought to counteract* the action of copper, to straighten the lattice and to *decrease its resistance* to the electric current when simultaneously present in the solid solution.

As soon, however, as these elements are precipitated in the form of  $Mg_2Si$  crystals, the action of copper becomes uncounteracted and the resistivity increases.

The increased chemical resistivity of self-aged duralumin can also be easily explained on the basis of the  $Mg_2Si$  precipitation. The latter is known to be very active chemically and the exposed surface of the metal becomes therefore attacked at the ultra-microscopical grainlets of this compound. Tiny specks of films of magnesia and silica are formed in these spots and, as they are non-conductors, all electrochemical action ceases; the metal becomes an electrochemically homogeneous substance.

Most of the investigators on the theory of duralumin hardening generally study the electric properties during the ageing process. The same method is applied to the structural anneal, which takes place at temperatures higher than 200°. Another method examines the dimensional changes during the processes of ageing and annealing.

The technology of duralumin manufacture has been dealt with mainly by Grard in France, Cohn in Germany, and Merica in the United States.<sup>1</sup> Grard's investigations are

- <sup>1</sup> 1 1010 L. M. Cohn, Ver 2 Foerd d Gerwerbefleisses, Vol. 89, p. 693
- 2 1012 L. M. Cohn, Elektrotechnik und Maschinenbau, Vol. 30, pp. 809.
3. 1013. L. M. Cohn, Elektrotechnik und Maschinenbau, Vol. 31, p. 430.
4. 1020 Grard, Revue de Metallurgie, Vol. 17, p. 286.
5. 1021. Grard, Revue de Metallurgie, Vol. 18, p. 567.
- 6 1922. Merica, Waltenberg, Finn U S. Bur Stds, Tech Papers, 132.
- 7 1922. Sander and Meissner, Zeitschrift fur Metallkunde, p. 17.

covered by Figs. 73, 74, 75, 76 and 77. The first two show the effects of the reduction by rolling upon duralumin stock in the direction of rolling and crosswise. Fig. 75 shows the effects of the annealing temperature upon the rolled alloy; Fig. 76, the fluctuation in mechanical properties during ageing;

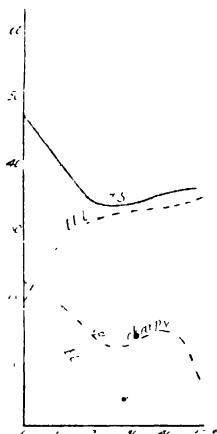


FIG 73  
(Tested lengthwise)  
Effects of cold rolling upon the mechanical properties of the raw duralumin sheet.

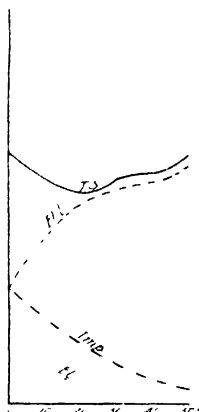


FIG 74  
(Tested crosswise)

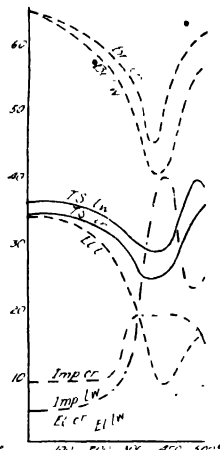


FIG 75. Effects of different annealing temperatures followed by furnace cooling upon the mech properties of raw duralumin sheet. (l.w.-samples taken lengthwise, cr-crosswise)

and Fig. 77, the influence of the temperature from which the rolled metal was quenched. The plotted scale is in thousand pounds per square inch for ultimate strength and elastic limit, in percents for elongation, Brinell numbers (at 500 kg. with 10-mm. ball), and in ft. lbs. for the Charpy impact values.

Fig. 78 gives the results of experiments by L. Guillet and his co-workers, who subjected strips of already aged duralumin to an ingenious quenching test, ascertaining the temperatures at which the final hardness is at the minimum. The strips were heated to 520° and 490° respectively at one end, and the

temperatures were taken at different points of the strip. Another series of experiments with strips quenched first from  $510^{\circ}\text{C}$ . and then heated non-uniformly by the application of  $310^{\circ}$  and  $210^{\circ}$  respectively at the hot ends has shown that

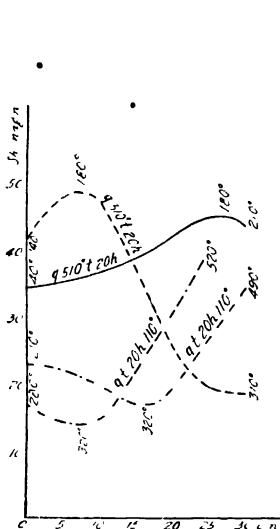


FIG. 78 Effects of quenching temperature upon the Sh. hardness of duralumin tempered for 20 hours at  $110^{\circ}$ , also effects of tempering temperature upon Sh. hardness of duralumin quenched from  $510^{\circ}$  (q-quenched, t tempered).

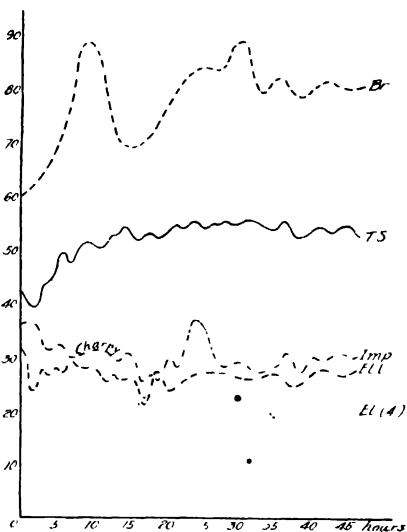


FIG. 79. Oscillation of the values of mechanic properties of duralumin during the first 4 days of ageing at normal temperature.

the highest hardness is obtainable at  $180^{\circ}$ . This figure represents, of course, only the best conditions for high scleroscope hardness, and may not be equally advantageous for other and more valuable properties.

Finally, Fig. 79, according to Cohn, shows the effect of reduction by further cold rolling upon the ultimate strength, yield point and elongation of different grades of duralumin. (We reproduce Cohn's data in the form of four curves for the increase of ultimate strength due to rolling). Cohn studied a

number of different "grades" of duralumin but did not state the corresponding compositions.) For the sake of completeness, we have to add that the highest strengths are obtained by increasing the amount of copper up to 5% , while the lowest correspond to 3.5% copper; the medium grades contain an increased amount of manganese.

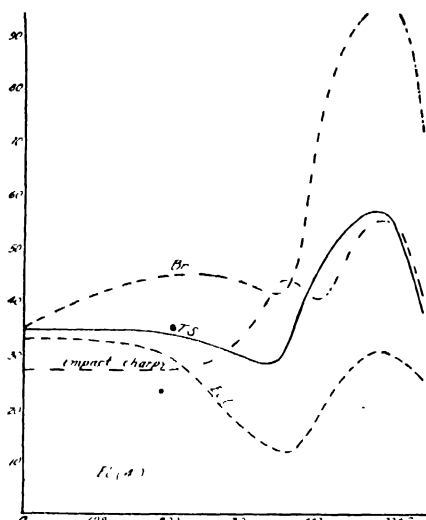


FIG 77. Effects of quenching temperature upon the mech properties of normally aged duralumin

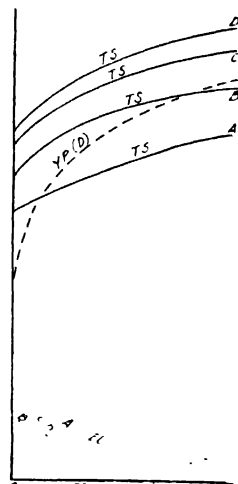


FIG 79 Effects of cold work upon the strength and ductility of different grades of duralumin

Cohn's work is the more interesting for the technologist in that it contains abundant data on the adaptability of duralumin for electric suspension cables and for girder construction. He also made extensive tests on the corrosion of duralumin under strain and under repeated exposure to low temperatures; he proved that duralumin composition is undoubtedly the most resistant under adverse conditions.

It is an interesting fact, that if the highest strength and hardness are desired (85,000 lbs./inch<sup>2</sup> and 160 Brinell), the alloy has to be self or heat aged first, and this treatment made complete before rolling or drawing is resorted to. If rolled at

some intermediate stage or right after quenching the ultimate values fall out too short. The heat-aged alloys do not permit more than 10–20% reduction in cold work.

Investigations by the British National Physical Institute dealt with the possibility of obtaining alloys of the duralumin type with zinc either as a substitute for copper or as an addition to it. An alloy with a base of 2.5% copper plus 18% zinc was developed, containing also about 0.5% magnesium and manganese; this was found to be still more responsive to heat treatment than the regular duralumin composition ("Alloy G"). These alloys age more quickly, require lower quenching temperature, and afford much higher strengths. Their chemical resistance, however, proved insufficient, and all such alloys containing over 10% zinc and some with even less, had to be discarded.

Quite recently, numerous experimenters have aimed to introduce less complex alloys as substitutes for duralumin, the numerous compositions of which are closely covered by patents. Such an alloy, "Aludur," containing neither copper nor manganese but only about 1.5 to 2.0%  $Mg_2Si$  was introduced in England. Other experimenters are working with the plain aluminum-copper alloys.

In short, if we wish to obtain a good heat-treatable alloy with constant properties, we cannot escape an aluminum-copper-magnesium composition. Copper by itself, if added to aluminum up to 6%, undergoes the whole line of changes related to duralumin and also produces an alloy of high strength, high ductility and even better rolling qualities. Without magnesium it becomes necessary to resort to tempering at 110° C. at least, because a simple ageing does not produce increased hardness and strength. The presence of small amounts of magnesium makes it possible to use much less copper and to get the desired properties with a higher degree of constancy. It must be added, however, that the whole question of pure aluminum-copper alloys and their heat treating remains uncertain. Some investigators obtained very good results while others could not get more than mediocre strengths and duc-



tility. The simultaneous presence of magnesium and copper seems to protect the solid solution during the quenching period while accelerating the reactions of the ageing process.

No brand of duralumin or analogous alloy (most of them proprietary) limits itself to the use of copper and magnesium alone. An addition of manganese is characteristic of the duralumins proper, while the addition of iron, nickel, or chromium, and possibly cobalt, produces other valuable alloys of the heat-treatable group. The alloy with 2% nickel requires more painstaking manufacture than the straight copper-magnesium-manganese composition, and does not yield equally high strengths on ageing or tempering. The finished alloy, the British "Y," is highly resistant to corrosion, however, and retains a good strength up to 350° C. An addition of chromium or cobalt might act like nickel, and may be used in connection with the latter or by itself. An alloy containing chromium and manganese is the subject of a U. S. patent. An addition of 1% nickel and 1% chromium, if properly handled, should give an alloy analogous to the "Y" type but with a still greater strength at higher temperatures.

More recently two new groups of heat-treatable alloys have been introduced in the trade, particularly in Germany. One of them belongs to the Al-Cu-Si system of ternary alloys. It contains only one member, the so-called "Lautal" (produced at the Lauta plant of the German Aluminum Company). Lautal has a definite composition of 4% copper and 2% silicon. The absence of magnesium makes it non-ageable; the silicon present stays in part in solid solution, but appears also at the grain boundaries of the ground mass reinforcing them in the same way as do the aluminides of manganese, iron and nickel in duralumins.

The second group is called "scleron-alloys." They always contain lithium as an age-hardening promoting factor, besides variable amounts of copper and zinc. This group of alloys is used both as cast and in the wrought state.

The strength of Lautal is not as high as that of regular duralumin but, granted a pure grade of aluminum metal (with

minimum amounts of iron), its manufacture becomes very easy and the properties rather stable. The Aluminum Company of America produces an alloy N° 25S which is very similar to "Lautal."

The Sclerons are alloys of a high strength (not much below the best grades of duralumin). They are probably cheaper to make than duralumin. The presence of zinc may, however, lead to a much lower corrosion resistance.

### ALUMINUM ALLOYS FOR HIGH-TEMPERATURE WORK

In many cases, machine parts made of aluminum have to withstand temperatures running up to 400° C. Pure aluminum and the most generally used plain alloys suffer a great loss of strength at temperatures as low as 100° C., while at 200° the decrease in strength becomes quite dangerous. A systematic investigation in this direction was undertaken under the auspices of the Sub-Committee for Light Alloys of the British Committee of Air Navigation. The first reports were printed in 1921 and, while they are not conclusive and in many cases the facts do not seem to indicate easy melting and casting practice, they contain much substantial information.

The old European alloys with an aluminum-zinc base were found to be entirely unsuitable for improvement. Their strength diminishes in an almost straight line from the comparatively high figures at normal temperatures, and no alloying can help them materially. This drop in strength seems to be an inherent property of the aluminum-zinc solid solution and it is quite possible that, due to the large size of the grains in this alloy, the intergranular strengthening obtainable by the use of elements forming aluminides is not sufficient to improve the alloy.

The aluminum-copper alloys were found to be the most adaptable to improvement by further alloying; any of the alloys with 8 to 14% copper can be benefited by a further alloying with up to 2% iron, 1% manganese, or 3% nickel as shown in Figs. 80 and 81. Nickel, although the most ex-

pensive, seems to be most effective, as it always increases the strength, can easily be introduced in quite substantial amounts, and does not affect the heat conductivity, a very important factor in the construction of light weight gas engines, etc. Manganese also acts quite advantageously, particularly in that it makes the alloys stronger at 250° than they are at normal temperature. This statement, however, requires corroboration, as the strength figures obtained by the experimenters on the Al-Cu-Mn alloys at normal temperature were undoubtedly

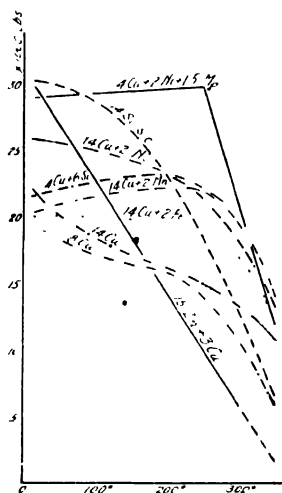


FIG 80 Effects of temperature upon the strength of different aluminum alloys in the chill-cast, and of silumin in the sand-cast state.

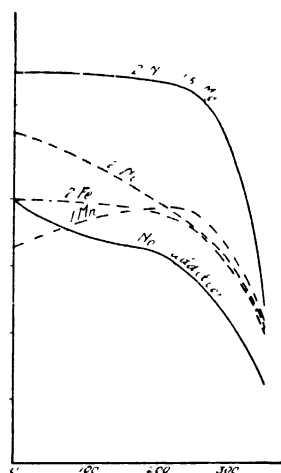


FIG 81 Effects of temperature upon the strength of the alloy "Americap # 12" or "British L 5" plain and strengthened by different additions

lower than those obtainable with plain aluminum-copper alloys under good casting practice. It does seem certain that no further improvement is obtainable by adding over 1% manganese. Manganese adversely affects the heat conductivity, reducing it at least by 25 percent.

A still greater improvement is obtainable in both sand-cast and chill-cast states by a simultaneous addition of 2% nickel plus 1 to 1.5% magnesium to the regular alloy No. 12,

and also to any alloy up to 14% copper. There is no need, however, to leave the copper so high unless a very high machineability is required, because alloys with only 4% copper and the same additional amounts of nickel and magnesium show practically the same strength. The alloys containing both nickel and magnesium are particularly interesting in that their elastic limit increases with temperature up to 200° C. The alloy 4Cu, 2Ni, 1.5Mg, called either "Y" or "Magnalite," is the more interesting because it is amenable to heat treatment in either a plain (heating and air cooling) or a more elaborate way; very high strengths, up to 40,000 pounds, are obtainable in the sand-cast state. Furthermore, the copper alloys improved by nickel and magnesium exhibit a higher chemical resistance than the plain binary and many ternary aluminum alloys.

More recently, experiments have been undertaken in the United States by E. Dix, Jr., and A. Lyon, with the idea of improving regular aluminum-copper alloys by additions of silicon, or of regular aluminum-silicon alloys by the addition of copper. These experiments have not yet reached a final stage. An interesting curve for an alloy containing 4% Cu and 6% Si is given in Fig. 80. This composition seems to retain its strength up to 150° C., and it is quite possible that alloys with 3 to 4% copper and from 10 to 12% silicon may prove still better as to chemical resistivity and strength at high temperatures than some of the other previously recommended alloys.

Cobalt and chromium have also been examined as aluminum strengtheners for high-temperature work. The results obtained by the British investigators of the casting alloys were rather inconclusive. It is very probable that chromium will afford a pronounced strengthening provided a method can be found to introduce it into aluminum in a rather highly dispersed condition and at a low temperature. In wrought alloys, the effects of chromium seem to be positive, although corroborative data are still wanting.







**PART IV**  
**ALUMINUM AND CORROSION**





## ALUMINUM AND CORROSION

ALUMINUM, like any other common metal used in the arts and industries, may come into temporary or constant contact with gaseous and liquid media. The first embrace pure and contaminated air, sulphurous gas, hydrogen sulphide, carbon dioxide, steam and various gas-vapor mixtures; the second, water, aqueous solutions of acids, alkalies and salts, organic chemicals, fused salts and fused elements (sulfur). Each of these substances is likely to develop a certain action upon the metal; a knowledge of the nature and scope of such action is therefore absolutely necessary for understanding the behavior of the metal in the uses to which it may be put. •

In the light of present-day knowledge, the phenomena of interaction of a metallic element with the surrounding media are understood as follows:

When a metal comes into contact with an active gaseous substance, a state of electric tension develops between them and this tension becomes relieved by the formation of a compound. The velocity of this reaction, *i.e.*, the attack of the gas upon the metal, depends upon the state of ionization of the gas. Dry oxygen, almost non-ionized, attacks metals rather slowly, while the highly ionized chlorine acts much more quickly. Humidity or increase in temperature leads to a stronger ionization in every case, the velocity of attacks being increased also.

### CHEMICAL ACTIVITY OF ALUMINUM

Aluminum is one of the most active elements. Commercially used aluminothermic processes alone give evidence of this fact. The table below shows the heat effects accompanying the combination of a few common metals with various elements and radicals, calculated per gr. equivalent of the latter.

TABLE V.—HEAT OF FORMATION (IN CALORIES) OF VARIOUS SIMPLE METALLIC COMPOUNDS

## I—IN THE ANHYDROUS STATE

For the Element; Per gr.— Equivalent of	Sodium	Aluminum	Iron	Copper	Silver
	Formula	Formula	Formula	Formula	Formula
	Heat of formation	Heat of formation	Heat of formation	Heat of formation	Heat of formation
Oxygen $\frac{O}{2}$	$\frac{Na_2O}{2}$ 51.0	$\frac{Al_2O_3}{6}$ 63.5	$\frac{Fe_2O_3}{6}$ 32.6	$\frac{Cu_2O}{2}$ 22.0	$\frac{Ag_2O}{2}$ 3.5
Hydroxyl OH	$\frac{NaOH}{1}$ 68.2	$\frac{Al(OH)_3}{3}$ 65.5	$\frac{Fe(OH)_3}{3}$ 33.7	$\frac{Cu(OH)_2}{2}$ 2	$\frac{Ag(OH)_2}{2}$ 2
Chlorine Cl	$\frac{NaCl}{1}$ 97.9	$\frac{AlCl_3}{3}$ 53.0	$\frac{FeCl_3}{3}$ 32.1	$\frac{CuCl_2}{2}$ 25.7	$\frac{AgCl}{1}$ 20.0
Sulfur $\frac{S}{2}$	$\frac{Na_2S}{2}$ 44.6	$\frac{Al_2S_3}{6}$ 21.6	$\frac{FeS}{2}$ 12.0	$\frac{Cu_2S}{2}$ 10.2	$\frac{Ag_2S}{2}$ 1.5

## II—IN AQUEOUS SOLUTIONS

	Sodium	Aluminum	Iron	Copper	Silver
	Formula	Formula	Formula	Formula	Formula
	Heat of formation	Heat of formation	Heat of formation	Heat of formation	Heat of formation
Cl—+aqua	$\frac{NaCl}{1}$ 96.6	$\frac{AlCl_3}{3}$ 70.4	$\frac{FeCl_3}{3}$ 42.6	$\frac{CuCl_2}{2}$ 31.3	$\frac{AgCl}{1}$ —
$\frac{SO_4}{2}$ +aqua	$\frac{Na_2SO_4}{2}$ 164.3	$\frac{Al_2(SO_4)_3}{6}$ 146.5	$\frac{Fe_2(SO_4)_3}{6}$ 108.4	$\frac{CuSO_4}{2}$ 98.7	$\frac{Ag_2SO_4}{2}$ 81.3
$\frac{NO_3}{1}$ +aqua	$\frac{NaNO_3}{1}$ 100	$\frac{Al(NO_3)_3}{3}$ 2	$\frac{Fe(NO_3)_3}{3}$ 52.4	$\frac{Cu(NO_3)_2}{2}$ 40.6	$\frac{AgNO_3}{1}$ 23.0

It is at once apparent that a combination with aluminum leads to effects far exceeding those developed in the case of iron, to say nothing of copper. From a purely chemical standpoint no stability whatsoever against corrosive attacks could be expected for aluminum.

#### . THE PASSIVITY OF ALUMINUM METAL

And yet metallic aluminum is much more resistant to corrosion than iron under practically any circumstances. To some extent it is even more resistant than copper. The only possible explanation of this fact lies in the formation of a protective film or skin. The slight but quickly forming tarnish upon a newly polished surface of aluminum is the first evidence of this film.

Taking into consideration the ubiquity of air and the inactivity of nitrogen, one cannot fail to conclude that this protective film consists of aluminum oxide. •

The formation of this film, it is well known, proceeds much more quickly when water or its vapor is present. The second conclusion is, that the oxide is probably hydrated to some extent. This agrees with the fact that aluminum forms a number of more or less definite hydroxides. Still the actual nature of this protective film is unknown, and while it certainly is an oxide, its state of hydration is open to discussion.

When aluminum, previously exposed to the air and in this or some other way covered with a film of oxide, comes into contact with a gas or vapor, the followings things may logically be expected to happen:

1. The film will be chemically attacked, converted into some other compound, peel off the metal and expose it to a vigorous attack. This occurs when the metal comes in contact with haloids and halogen acids, particularly in the humid state. •

2. The film is not attacked but made more gelatinous (peptized). The attacking medium finds a way through the weakened film and attacks the metal. Vapors of formic acid and certain organic substances containing chlorine act defi-

nately in this way. Hot saturated steam comes in the same class.

3. The film remains solid and non-penetrable to a great extent. This happens in the case of low temperature steam, hydrogen sulfide, sulfur and carbon dioxide, ammonia, vapors of acetic acid, organic amines, etc.

From the industrial standpoint the question of the attack by gases and vapors is simple. Substances of the third group may be safely allowed to come into contact with aluminum, while those of the second and particularly of the first group must be prevented from touching its surface for any length of time.

#### CORROSION BY LIQUID SUBSTANCES

This type of corrosion is always more severe than that by gases and its occurrence so frequent, that it must be carefully considered in any given case. Most important are cases where aluminum is attacked by aqueous solutions of acids, alkalies and salts. Here the inherent activity of aluminum is matched against its ability to form, retain and rebuild a protective skin.

The theory of the mechanism of the corrosion of metals by liquids and aqueous solutions is still in its infancy. There is not yet enough fundamental quantitative information accumulated to treat the subject in an exhaustive manner. The starting point of the present-day hypothesis is the well-corroborated assumption that a metal may or may not react with a solution carrying ionized solutes, according to the relative position of the metal and the cation under consideration in the electrochemical series. This latter as reproduced in the table below shows that, with the exception of the alkaline and alkaline earth metals, aluminum has the highest potential among the common metals.

The electrochemical theory also requires that immediately after the attack is initiated, due to the potential difference between the metal and the cations present in solution, the surface of the metal assumes a charge of an opposite sign (polariza-

TABLE VI.—POTENTIALS OF VARIOUS METALS AGAINST THE NORMAL HYDROGEN ELECTRODE AND THEIR IONIZATION HEAT EFFECTS

<i>Metal</i> <sup>•</sup>	<i>Volts</i>	<i>Remarks</i>	<i>Calories per Gr. ion equivalent</i>	<i>Metal</i>	<i>Volts</i>	<i>Calories per Gr. ion equivalent</i>
Lithium	+3.0			Nickel	0.22	8.0
Potassium	2.92	Approx.	+61.8	Lead	0.12	0.2
Barium	2.82	"		Tin	0.1	1.7
Sodium	2.8	"		Hydrogen	0.00	
Strontium	2.72	"	57.4	Antimony	0.25	
Calcium	2.52	"	60.0	Bismuth	-0.30	
Magnesium	1.55		54.7	Copper	-0.34	-16.0
Aluminum	1.27		54.5	Molybdenum	0.60 <sup>2</sup>	
Manganese	1.05?		40.3	Palladium	0.77	
Zinc	0.75		25.0	Silver	-0.79	-25.0
Molybdenum	0.70 <sup>1</sup>		17.6	Tungsten	-0.80 <sup>2</sup>	
Chromium	0.65 <sup>1</sup>			Mercury	-0.86	-20.0
Tungsten	0.60 <sup>1</sup>			Platinum	-0.86	
Iron	0.43		11.0	Gold	-1.08	
Cadmium	0.40		9.0	Chromium	-1.19 <sup>2</sup>	
Cobalt	0.30		8.5			

<sup>1</sup> On a perfectly clean surface (highest activity).<sup>2</sup> Metal covered with film (highest passivity).

tion), further dissolution being arrested. In cases where hydrogen is the anion, its bubbles may stick to the metal and due to their own charges add to the polarization voltage of the metal a certain *over-voltage*. This latter also counteracts further dissolution.

Experience shows, however, that all corrodible metals continue to dissolve and this fact leads to the creation of another hypothesis suggesting that such metals always carry certain impurities, which no matter how small in quantity form a large number of *local electrochemical couples*. These latter are assumed to be responsible for setting up local currents and causing the dissolution of either the main metal or the impurity itself. In the particular case of aluminum, the latter is almost always bound to dissolve, leaving behind the impurity to promote further electrolytic corrosion.

Regardless of the correctness of the complicated (single potentials, polarization voltage, over-voltage, localized electrolytic couples, etc.) electrochemical theory of corrosion, the fact remains that nobody has so far succeeded or tried to develop an experimental technique and methods of logical analysis permitting the study of corrosion phenomena in the light of this theory. In consequence it becomes necessary to approach the problems of corrosion from an entirely different standpoint.

#### ESSENTIAL FACTORS IN CORROSION PHENOMENA

In each case of continuous attack upon a metal by a liquid medium taken at the moment when a stationary state of dissolution is established, the amount of metal dissolved per unit area and time must depend logically upon the following factors: (1) the sum total of the velocities with which the ions of the dissolved metal move away from its surface and the ions and molecules present in the attacking solution move toward the same, (2) the saturation point of the layer of the attacking liquid in contact with the metal, and (3) the thickness of this layer. With these three factors known, the problem of corrosion in each practical case might be dealt with on the

basis of a strictly correct and exact calculation. No resort to any complicated fundamental theory would have been required.

#### TESTING ALUMINUM AND ITS ALLOYS FOR CORRODIBILITY

So far we do not possess knowledge of the three magnitudes mentioned even for one definite case. Therefore the only practical conclusion remains, that the velocity of corrosion "equals itself" and accordingly has to be found by means of a direct test.

This testing may be qualitative or quantitative or both. In the qualitative test one presumes that two test pieces showing a substantial difference of corrodibility by a medium taken as a standard, probably will show corrosion of the same order in a majority of other cases. A qualitative test is quick and may furnish a fair insight into the chemical character of a given piece of metal. If, however, one has to select metals or alloys in the design of an apparatus or structure requiring a high factor of safety or to calculate the safe thickness of a piece subjected to the attack, a quantitative test presents the only way out.

One of the best known qualitative tests was suggested by Mylius (*Z. Metallkunde*, v. 14, p. 293, 1922). As described at an earlier occasion (page 10) it consists in the immersion of a standard surface ( $20\text{ cm}^2$ ) in a given amount of hydrochloric acid ( $20\text{ cm}^3$ ) contained in a small round-bottomed flask of a standardized size. Under these conditions the increase in the temperature of the acid indicates reasonably well the velocity of dissolution. The presumption is that the same piece of metal will show nearly the same order of corrodibility in a general way.

A sample to be used for the Mylius test is usually finished by grinding the metal on paper N<sup>o</sup> 00 or N<sup>o</sup> 000, and after having been first freed from greasy substances by a dip in hot sodium hydroxide solution is immediately immersed in the acid.

One factor militates strongly against the Mylius test,



namely, the automatic increase in the corrosion velocity due to the increase in temperature. Accordingly, the recorded increase in temperature for an alloy showing a pronounced heat effect in the reaction will be larger than the actual increase due to the chemical activity of the reagent.

### QUANTITATIVE TESTING

Very little attention has been paid so far to this phase of testing aluminum and its alloys. Some data are already available on the corrodibility of aluminum in its highest (99.7%) and average (99.0%) commercial grades by nitric acid of various concentrations, by commercial nitric acid of 1.42 sp. gr. at various temperatures, by cold and boiling acetic acid and by some fatty acids such as propionic and butyric.

Most of these data are due to Seligman and Williams (J. S. Ch. Ind.), and while being far from adequate, they are the only ones on which calculations and specifications may be based governing the use of aluminum in certain fields of the chemical industry. These data, with the supplements added from time to time by various workers for different corrosive media, are summarized in the two tables below.

### THE INFLUENCE OF IMPURITIES AND ALLOYED ELEMENTS

Considering our fragmentary knowledge of the corrosion of commercial grades of aluminum, it is not surprising at all that the study of the more complicated alloys has hardly been touched. In this field the most astonishing combinations of ideas prevail. But no matter how little useful information is available, it is imperative to clear up the situation to some extent.

All impurities and definite additions which obtain in aluminum alloys fall into either of three groups:

1. Non-metallic impurities.
2. Components giving rise to intermetallic compounds or appearing as elementary secondary constituents in the metal.
3. Components going into solid solution in the grains of the main metal.

TABLE VII.—CORROSION LOSSES BY STRICT DISSOLUTION IN VARIOUS MEDIA OF THE PUREST GRADE OF COMMERCIAL ALUMINUM (99.8%) (PITTING NOT TAKEN INTO ACCOUNT)  
(GRS., M<sup>2</sup>. DAY; NO ARTIFICIAL MOVEMENT OF LIQUID)

Medium	Concentration or sp. gr.-ly.	Temperature	Loss	Source of Information
Hydrochloric Acid	10%	24° C	1200-1500	Corson
	6.5	0°-22°	1.30	Harada
	9.9	20°	0.012	Seligman and Williams
	9.6	"	0.46	"
	9.1	"	.30	"
	8.9	"	.91	"
	7.0	"	3.10	"
	7.0	27°	7.00	"
	6.5 (1.4)	0°	0.6	"
	"	10°	1.3	"
	"	20°	4.8	"
	"	30°	11.0	"
	"	40°	21.0	"
	"	50°	45.0	"
	"	60°	93.0	"
	"	70°	175.0	"
	"	80°	345.0	"
	80° ± 3°		370.0	Corson
	"	90°	630.0	"
	"	100°	1080.0	S. and W.
	"	110°	1580.0	"
	"	120°	2100.0	"

TABLE VII. — CORROSION LOSSES BY STRICT DISSOLUTION IN VARIOUS MEDIA OF THE PUREST GRADE OF COMMERCIAL ALUMINUM (99.8%) (PITTING NOT TAKEN INTO ACCOUNT) — Continued  
(GRS. M<sup>2</sup> DAY; NO ARTIFICIAL MOVEMENT OF LIQUID)

Medium	Concentration or sp. gr.-ty.	Temperature	Loss	Source of Information
Nitric Acid	60',	27°	12.00	S. and W.
	56	20°	4.10	"
	50	27°	18.4	"
	46	24°	12.5	Corson
	44	20°	5.60	S. and W.
	40	27°	20.0	"
	30	27°	18.0	Corson
	23	24°	11.60	"
	22	80° ± 5°	7.0	"
	9.3	20°	3.10	S. and W.
	4.4	20°	0.60	"
	0.5	15°?	1.83	Harada
	100 + 0	20°	12.5	S. and W.
	60 + 10	"	18.0	"
	80 + 20	"	18.0	"
(1.84 Sulfuric + 1.42 Nitric) (Mixed Acid)	20 + 30	"	18.0	"
	60 + 40	"	18.0	"
	50 + 50	"	18.0	"
	40 + 60	"	17.5	"
	30 + 70	"	15.7	"

Sulfuric Acid	20 + 80	"	11 7	"
	10 + 90	20°	7 0	"
	0 + 100	20°	1 6	"
	0.5	15°	1 27-1 40.	Harada
	5%	25°	16 1	?
Acetic Acid	10%		30 0	?
	20%		23 1	?
	absolute		> 700	
	60 0	boiling	0 70	S. and W.
	99 2	boiling	0 00	"
	98 0	20°	0 00	Corson
	98 0	boiling	3 50	S. and W.
	90 0	20°	0 023	"
	90 0	boiling	17 0	"
	80 0	boiling	30 0	"
	70 0	boiling	33 6	"
	60 0	20°	0 070	"
	60 0	boiling	41 4	"
	50 0	24°	1 0	Corson
	50 0	80 ± 3°	12 0	"
	50 0	boiling	42 0	S. and W.
	40 0	boiling	50 5	"
	30 0	boiling	50 5	Harada
	20 0	15°?	53 5	"
	20 0	15°?	53 5	S. and W.
	10 0	20°	0 092	"
	10 0	boiling	60 0	Harada
	5 0	15°	0 12	"
	5 0	15°	62 0	"

TABLE VII. — CORROSION LOSSES BY STRICT DISSOLUTION IN VARIOUS MEDIA OF THE PUREST GRADE OF COMMERCIAL ALUMINUM (99.8%) (PITTING NOT TAKEN INTO ACCOUNT) — *Continued*(GRS. M<sup>2</sup> DAY; NO ARTIFICIAL MOVEMENTS OF LIQUID)

Medium	Concentration or sp. gr.-ly.	Temperature	Loss	Source of Information
Acetic Acid	1.0%	20°	0.115	S. and W.
	1.0	boiling	123.0	"
	0.5	20°	0.138	"
Propyonic Acid	0.2	boiling	78.0	"
	absolute	boiling	20000.0	"
	99	boiling	0.5	"
Butyric Acid	80	boiling	27.0	"
	absolute	boiling	1200	"
	80	boiling	2.7	"
Ammonia	0.5	15°?	1.83	Harada
Sodium Hydroxide	11.0	24°	265.0	Corson
Carbon Dioxide	Sat-d solution	15°?	0.026	Harada
Sodium Chloride	3	15°?	0.034	"
Sodium Sulfite	3	15°?	0.046	"

TABLE VIII. — CORRODIBILITY OF SECOND GRADE ALUMINUM SHEET (99.0% Al, 0.7% Fe)

Attacking Medium	Concentration, %	Loss in gms./m <sup>2</sup> day	Remarks
Hydrochloric acid	0.37	1.0	Annealed (Maass and Wiederholt. Z. Metallkunde, 1925, V. 17, p. 115)
	10	2100	Well annealed
Nitric acid	10	3200	Hard rolled
	0.63	0.8	(M. and W.)
	23	320	At 24° C. well annealed (Corson)
Sulfuric acid	23	370	" hard rolled ( " )
Sulfurous acid	0.5	0.7	(M. and W.)
Oxalic acid	1.5	1.0	"
Tartaric acid	4.5	0.065	"
Acetic acid	7.5	0.045	"
" "	60	0.090	"
" "	50.0	13.5	(At 80° C.) annealed (Corson)
" "	50.0	18.5	" hard rolled ( " )
" "	50	42	Metal annealed, acid boiling (Seligman)
" "	60	40.5	" " " "
" "	70	33	" " " "
" "	80	20.5	" " " "
" "	90	16.5	" " " "
" "	90.0	3.5	" " " "
" "	99.0	0.7	" " " "
Potassium hydroxide	0.06	0.85	(M. and W.)
Sodium hydroxide	0.04	0.50	"
Lime	0.15	0.55	"
Baryta	2.5	0.22	"
Ammonium chloride	10.7	0.23	"
Sodium carbonate	10.7	0.32	"

The first class of impurities, of course, are never intentionally added. They form in the process of melting and pouring and then remain in the alloy in the shape of grainlets or films. While quite undesirable from the standpoint of strength, they are more or less harmless from the standpoint of chemical resistivity, if not so large or soluble as to form channels through which the corroding medium may penetrate deep into the metal. Being non-conductors they do not start any electrolytic action and cannot therefore accelerate the corrosion. On the other hand, if corrosion is taking place due to other factors, these films or particles of non-metallic substances will cause pieces of the metal to crumble out, undermining the strength of the whole article.

Those additions, which form intermetallic compounds or remain in the alloy as individual elementary constituents, must undoubtedly tend to start local currents and add to the corrosion. With additions (or the constituents formed from them) electrochemically more noble than aluminum, the total mass of the metal undergoes an accelerated corrosion until all phenomena involved, for instance, polarization, over-voltage, etc., acting together result in a certain constant velocity of corrosion. Corrosion will tend to eliminate secondary constituents of a higher electrochemical potential than aluminum, either by dissolving them or converting them into oxides or insoluble salts. Although these latter are not beneficial to the strength of the metal, they do not exert any undesirable chemical influence.

Comparing various additions usually made to aluminum, we find the following range of electrochemical potential differences between them and aluminum metal (see Table IX):

If present as elements, almost all of these additions, with the probable exception of manganese and silicon, would undoubtedly cause strong electrochemical action. In fact, few of them remain uncombined, the majority forming aluminides of various compositions. Frequently, two or three, and sometimes more, aluminides appear between pure aluminum and the pure additional metal. There exist no experimental data

TABLE IX

Potential differences between various additional elements used in aluminum alloys and aluminum metal.

Magnesium	+ 0.28 volt	Iron	— 0.84 volt
Beryllium <sup>1</sup>	— 0.15 "	Cobalt	— 0.97 "
Aluminum	0.00 "	Nickel	— 1.05 "
Silicon <sup>1</sup>	— 0.02 "	Tin	— 1.17 "
Manganese	— 0.22 "	Antimony	— 1.52 "
Zinc	— 0.52 "	Copper	— 1.61 "
Chromium	— 0.62 "	Mercury	— 2.13 "

concerning the actual electrochemical drop from aluminum metal to each of the aluminides formed. It will not lead to a big error, however, if we grant that, in a system with one aluminide, the drop from the metal to this compound may be in the neighborhood of one-half the total electrochemical difference between the two metals. In systems with two compounds, the first drop may probably be in the neighborhood of one-third the total difference, etc. Proceeding in this manner, one may estimate the possible electrochemical differences between aluminum metal and the aluminides embedded in it to run as shown in Table X.

This table may explain why iron, a much less electrochemically noble metal than copper, may lead to more electrochemical action for the couple of aluminum — iron-aluminide than is possible for the aluminum — copper-aluminide couple. The same reasoning explains why the addition of tin may be bad and that of mercury entirely detrimental to the chemical stability of aluminum. No aluminide is formed in these cases and every particle of tin or mercury present as such will lead to a high difference in electrochemical potentials and to strong local currents.

<sup>1</sup> The figures for the Be-Al and Si-Al couples were roughly determined by the author using a high resistance voltmeter. The highest figure found for Si-Al (in normal hydrochloric acid) did not go above 0.01 volt and values much below it were found in saline and NaOH solutions. Silicon is always slightly more noble than aluminum. Beryllium is less noble in saline and acid solutions but more noble in sodium hydroxide. Still with the exception of the normal hydrochloric acid (0.15 volt) the figures do not fall above 0.05 volt.



TABLE X.—VOLTAGES OF LOCAL COUPLES FORMED BY ALUMINUM AND VARIOUS ALUMINIDES OR ELEMENTARY SECONDARY CONSTITUENTS FOUND IN ITS ALLOYS

Metal	Number of compounds in the binary series	Electro chemical couple formed by		Develops volts (probably)
		Anode	Cathode	
Magnesium	2	(Al Mg) solid solution	Al <sub>3</sub> Mg <sub>2</sub>	0 10
Beryllium	none?	Aluminum	Beryllium	0 10
Silicon	none	Silicon	(AlSi) solid solution	0 02
Manganese	2	MnAl <sub>3</sub>	Al	0 08
Nickel	3	NiAl <sub>3</sub>	Al	0 27
Chromium	1 (2?)	Cr <sub>3</sub> Al (CrAl <sub>3</sub> ?)	Al	0 20-0 30
Cobalt	2 (3?)	CoAl <sub>4</sub>	Al	0 25-0 33
Copper	4	CuAl <sub>2</sub>	(Al Cu) solid solution	0 35
Iron	1	Fe Al <sub>3</sub>	Al	0 40
Zinc	1 unstable	Zn	(AlZn) solid solution	0 52
Antimony	1	Sb Al	Al	0 75
Tin	none?	Sn	(Al Sn) solid solution	1 17
Mercury	none	Hg	Al	2 13

### INFLUENCE OF COPPER

In the third group, embracing the additions which enter into solid solution in aluminum, two different types of influence are also discernible. Thus, in the alloys of aluminum and copper the electrochemical potential must drop in some way from that of aluminum to that of copper and in the regions of single solid solutions this drop never occurs in jumps but proceeds in a continuous fashion. Solid solutions of copper in aluminum should then be somewhat more noble than aluminum itself, provided the copper is uniformly distributed. In other words, copper in small amounts must have an anti-corroding effect. To expect, however, that an addition of copper will materially improve the resistance of aluminum is unwarranted. In the stable state not more than 2% of copper by weight, or less than 1 atomic percent will enter into the lattice of aluminum. Current theories state, and practice supports the statement, that the first large improvement in the chemical resistivity of a given metal can be attained only at the point when 12%, or more, of the atoms of the main metal are substituted by those of the more noble metal. Even if the introduction of so much of copper (22% by weight) into solid solution should be possible, it is not sufficiently noble itself to exert much protective action on aluminum.

When copper is present to more than 2%, and in the absence of a suitable heat treatment, all excess copper forms copper aluminide and remains between the grains. This compound is more noble than aluminum and chemical action takes place at these boundaries. Pitting ensues and the particles of aluminide crumble away. Some loose copper remains on the surface of aluminum and accelerates corrosion.

### INFLUENCE OF MAGNESIUM

Magnesium, very frequently added to aluminum alloys and supposedly going into solid solution up to 10%, is slightly less noble than aluminum. To reach its higher potential level starting from that of aluminum, the alloys must pass through

a series of changes both continuous and spontaneous. • At the aluminum end, due to the presence of solid solutions, we must have a continuous increase in the electrochemical potential, and the alloy should, therefore, be less noble and probably be more likely to corrode. The difference of potential between pure aluminum and an aluminum-magnesium solid solution is, however, small in comparison with the single potential of aluminum and may not lead to an appreciable increase in corrodibility.

#### INFLUENCE OF ZINC

Zinc is by 0.52 volt more electrochemically noble than aluminum. According to the most reliable constitutional diagrams of the binary Al-Zn series 12% zinc at least and probably about 17% forms a stable solid solution in aluminum. This circumstance calls for a reasonable drop in the electrochemical potential of alloys located within this range. Harada's tests, however (see further), show definitely an universal increase in the corrodibility of wrought aluminum alloys containing even as little as 2% zinc. Higher amounts of zinc are still more detrimental to corrosion resistance particularly in the cast state.

The reason why the addition of zinc exerts an undesirable chemical influence upon aluminum is probably very complicated. The one causing cast Al-Zn alloys to be more corrodible is plain. It lies in the enormous differences in the chemical composition within each individual grain of the casting and the consequent variations of the electrochemical potential level all over the alloy.

With zinc contents above 17% the alloy will not show a uniform homogeneous state, no matter what its previous history. Free zinc will be always present in a visible or invisible state (ultramicroscopical precipitation during ageing) and cause accelerated corrosion.

#### INFLUENCE OF TIN

When present in the free state (eutectic tin) tin exerts a very bad chemical influence upon aluminum due to the big difference in the electrochemical potentials (1.17 volts). In

fact alloys containing free tin are absolutely unstable even under the action of plain tap water.

On the other hand it is rather strange that even small amounts of tin supposedly completely soluble in solid aluminum reduce the latter's corrosion resistance greatly and definitely. Theoretically something like 0.15 volt at least should have been detracted from the potential of aluminum in the presence of 10% tin. The fact of the corrodibility's increase simultaneously with the potential becoming more noble shows plainly that no simplified electrochemical theory of corrosion should be applied to the study of the corrosion of aluminum alloys.

As mentioned before, all components of an alloy naturally present, or intentionally added, are likely to start electrolytic action both when remaining as secondary constituents and when forming metallic compounds which appear as a separate phase. The largest number of metals usually added or found in aluminum belong to this class. Iron, nickel, manganese, cobalt, chromium, etc., all must act qualitatively in the same direction, *i.e.*, make the alloy less resistant. In the case of iron, we have a definitely established fact that purest commercial aluminum always shows a better resistance to chemical attack than any second grade aluminum which usually contains somewhere near .7% iron.

#### THE SEARCH FOR MORE RESISTANT WROUGHT ALLOYS

Although the metallic elements that have just been mentioned may adversely affect the chemical resistivity, a number of other influences and demands must be taken into account. The softness of pure aluminum renders it inconvenient for many uses. It shows besides a noticeable tendency to self-anneal and to lose strength. Again, the pure metal is too likely to fail by fatigue at the grain boundaries, inasmuch as they are not reinforced in any way. These mechanical defects call for improvements and the question remains as to the most desirable way of achieving this end, a question resolving itself into a search for suitable reinforcing agents.

About the first experiments along this line were made in

America by Merica, Waltenberg and Freeman (B. St., Tech. Paper N° 132). They subjected a number of wrought aluminum alloys, containing manganese, nickel, copper and magnesium either separately, or simultaneously, to the so-called salt spray test. In this test, sample strips are exposed to a jet of air carrying an atomized 10–20% salt solution. The experiments were not quantitative, the results being judged by the appearance of the strips at the end of the test. The alloys were classified into four groups, and, with a few exceptions, most of the alloys tested came into group N° 3 or N° 4, showing high corrodibility. The classification, as reproduced below, was not decisive enough to permit any conclusions about the positive or negative value of the given addition.

Alloy	Class of Corrodibility		
	As cold rolled	As annealed at 450° slowly cooled	As annealed at 500° and water-quenched
Second grade aluminum	4	3	3
1.1% manganese	3	3	1
2.4% magnesium	3	3	3
1.7% Mn + 2.0% Mg	1	3	1
3.2% copper	4	4	2
3.2% Cu + 0.5% Mg	4	3 — 4	1 — 2
3.4% Nickel	3	3	3
1.8% Ni + 2.0% Mg	3	3	3
3.5% Ni + 1.0% Mg	3	3	3

Analogous experiments were recently made in Japan by T. Harada (Mem. Col. Eng., Kyoto Uni., 1925, v. 3, N° 9), who studied the influence of small additions of copper, silicon, nickel, iron, cobalt, manganese, zinc, magnesium and tin upon the chemical resistivity of aluminum. The experiments were hardly systematic enough to result in reliable data. In the absence of more complete information, the results of Harada, as recalculated by the author, are reproduced in the table below. Fig. 82 shows the corrodibility of the investigated alloys by very dilute (0.5%) sulphuric, hydrochloric and nitric acids and ammonia. The corrodibility of pure aluminum was ex-

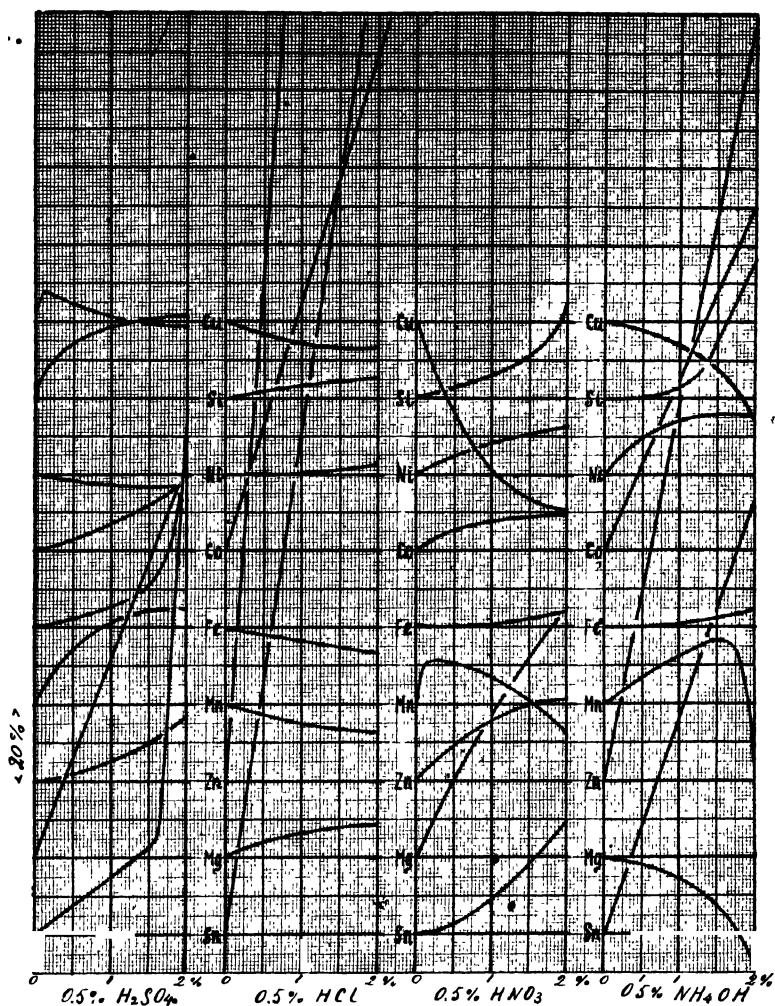


FIG. 82. Influence of small additions upon the corrodibility of wrought aluminum. One small division upon the ordinatâ represents 10% plus or minus.

trapolated from all the data and taken as 100. Harada presents also figures relating to the action of a saturated solution of carbon dioxide, and also of sodium chloride and sodium sulphite (3%). Both the table and the accompanying diagram show that no advantageous effect from other additions, besides

TABLE XI.—INFLUENCE OF ADDITIONS OF SMALL AMOUNTS OF VARIOUS METALS UPON THE CORRODIBILITY OF WROUGHT ALUMINUM IN VARIOUS AQUEOUS SOLUTIONS

Corrosive medium		0.5% $H_2SO_4$	0.5% $HCl$	0.5% $HNO_3$	0.5% $NH_4OH$
Loss of pure aluminum g./sq. day		1.24 g	1.30 g	1.74 g	1.84 g
Amount of addition	%	% Variation of Loss			
Copper	0.1	+7.5	±0.00	+3.0	+23.5
	1.0	+1.5	-6.5	-40.0	-7.5
	1.5	-0.5	-5.5	-47.0	-10.0
	2.0	-1.0	-6.0	-40.0	-25.5
Silicon	0.1	+7.5	±0.0	+2.0	+16.0
	1.0	+10.0	+3.0	+7.5	+2.5
	1.5	+21.0	+4.0	+9.5	+15.5
	2.0	+21.0	+5.5	+6.52	+37.0
Nickel	0.1	+1.0	+3.2	+12.5	+2.5
	1.0	-3.0	±0.0	+9.0	+14.0
	1.5	-3.0	-1.0	+9.5	+18.5
	2.0	-2.0	+5.0	+12.5	+14.0
Cobalt	0.1	+0.5	-3.0	-0.5	+6.5
	1.0	+6.5	+7.5	+13.0	+74.0
	1.5	+13.5	+90.0	+8.0	+56.5
	2.0	+19.5	+680.0	+7.5	+90.0
Iron	0.3	+1.5	-1.0	+5.0	±0.0
	1.0	+5.5	-4.0	-0.5	+0.5
	1.5	+10.7	-6.0	+2.0	-21.5
	2.0	+46.5	-6.0	+5.0	-6.5
Manganese	0.1	+3.5	+9.0	+13.5	±0.0
	1.0	+22.5	-6.0	+6.0	+12.5
	1.5	+24.0	-6.0	+3.0	+17.0
	2.0	+26.0	-7.5	-8.0	-15.0
Zinc	0.1	±0.0	+3.2	+0.5	+5.5
	1.0	+4.0	+270	+15.5	+202.0
	1.5	+9.0	?	+20.5	+266.0
	2.0	+18.0	?	+21.0	+311.0
Magnesium	0.1	+22.5	+24.0	+14.0	+26.0
	1.0	+40.0	+6.5	+40.0	-4.0
	1.5	+87.0	+7.0	+51.0	-10.0
	2.0	+103.0	+9.5	+66.0	-28.0
Tin	0.1	+6.5	+160.0	-1.5	+23.0
	1.0	+16.5	+135.0	+8.5	+55.5
	1.5	+22.5	+195.0	+18.0	+530
	2.0	+137.0	+475.0	+30.0	695

copper, can be expected. On the contrary, the injurious effects of most additions, particularly of tin, zinc, magnesium and cobalt, are at once apparent. In one case only, that of ammonia, magnesium shows an advantageous effect of noticeable magnitude. That copper does not show a definitely advantageous effect in sulphuric acid solution as found by Harada, may hardly be considered as fully established. It is also extremely doubtful if cobalt actually acts as recorded in opposition to the effects of nickel, iron and manganese. Should the data on cobalt be true, they may shed new light upon the process of grain refinement produced by additions of cobalt, as noticed by Shirmeister (see page 39).

#### THE IMPORTANCE OF THE PROTECTIVE FILM

In the practical utilization of aluminum, one can be certain that all acid substances will attack aluminum unless the alloy is covered with some kind of a protective film, or unless one forming during the first few moments of corrosion largely arrests further action. It is thus most important in the case of aluminum and its alloys to study their ability to form and to maintain a protective film.

In connection with this vital question, the author has made a few experiments, which, while few in number, always yielded identical results. The test consists in first studying the mechanism of the formation of the protective film, and then testing the velocity of its penetration, disruption or solution by various substances.

#### THE METHOD OF TESTING

The sample prepared by grinding on emery paper N° 0-N° 00 and washing with ether, is immersed in a warm (50° C) 2% solution of bichromate of sodium. There it is either touched by or firmly fixed to an aluminum anode, the cathode being another aluminum rod. A current of 110 volts D. C. passing through a number of 200 w. lamps in parallel and a recording ammeter is used. The more uniform the alloy, the quicker it becomes covered with an oxide film, the intensity of the current dropping and the lamps fading out. • Pure alumi-



num, if touched by the anode, practically stops the current in a few moments, the oxide film formed being perfect enough to act as a good insulator. Even with the better aluminum alloys, it takes a somewhat longer time for the lamps to fade out and the residual current shows a higher intensity. To form a reasonably good protective film in these cases, more time is needed. Alloys which definitely contain a secondary constituent in particles of large size, and those that are not uniform in the chemical structure of individual grains, require a great deal of time to become covered by the protective film, and the action of the current leads to the formation of a flocculent substance oozing out from the surface of the test piece.

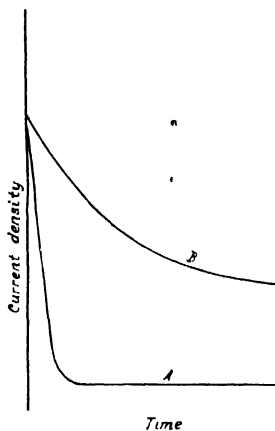


FIG. 83.

The test piece, covered in the manner described by a protective film, is next submerged in a solution of hydrochloric acid of a volume large enough to render concentration changes due to the dissolving of the metal negligible and prevent appreciable rise in temperature due to the heat developed. A graduate tube of 1 liter or so, full of the same acid, is fixed above the test piece so as to collect the hydrogen evolved, the amount of the latter being recorded either by direct reading or in some automatic

way. One may, for instance, introduce some red dye into the acid solution and fix the apparatus in such a way that a thin flat beam of light is sent through the graduate and through a slot behind it into a chamber where a revolving cylinder is covered with photographic paper. That part of the graduate occupied by the hydrogen transmits the light and forms a dark streak on the sensitive paper, while the red colored liquid stops the chemical action of the beam of light entirely. In this way, a faultless record of the attack may be obtained.

In direct relationship to the chemical and physical properties of the alloy the mechanism of the attack develops in the following way. The acid starts to penetrate the film, and the stronger and more uniform the latter is, the longer it takes for the acid to come into contact with the metal itself. A certain time usually elapses before an appreciable gas development is noticed. This period of time shows the stability of the protective film, and in addition to the current-time curves of the electrolytic passification process, it furnishes a means of judging the ability of the alloy in question to form a protective film, and to maintain it under given conditions of use.

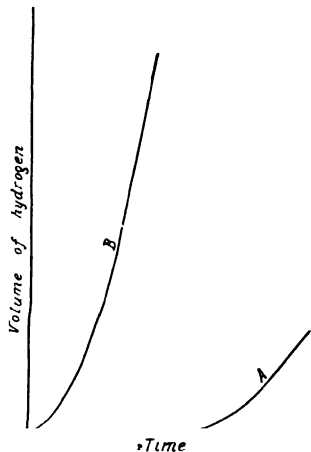


FIG. 84.

After the action begins, the process goes on with increasing velocity until the whole surface is laid bare and a constant velocity of hydrogen development is obtained. This constant speed is a direct result of the various forces playing upon the surface of the sample, and is strictly characteristic of the alloy. Grain size, uniformity of the chemical structure of the grain, presence of large grainlets of a secondary constituent at the grain boundaries, ultra-microscopic or fine microscopic precipitates within the grains due to processes of heat treatment and ageing, mechanical strains—all find expression in the results of the tests. Graphs A and B in Figs. 83 and 84 show the run of the curves of passification and solution for one high resistant and one low resistant alloy. The photographs on plates A, B, C, D, E show the comparative effect of 10% hydrochloric, 20% nitric and 50% acetic acid upon the surfaces of various alloys. The hydrochloric and nitric tests were made at 24° C., and the acetic acid tests at 80° C. Photographs showing the action of hydrochloric acids correspond generally to the development of 70 c.c. per cm<sup>2</sup> of the sample, which usually takes place

LIST OF SAMPLES SHOWING THE CORROSION EFFECTS OF 23% HNO<sub>3</sub> ACID (IN 24 H.) AND OF 10% HCL FOR 70 C.C. HYDROGEN PER CM<sup>2</sup>

Plates A, B, and C, D

No.	Alloy	State
1	Aluminum	2nd grade sheet, hard
2	Aluminum	2nd grade sheet, annealed
3	2% Mn, 0.7% Fe	Forged, annealed at 530°, quenched
4	5% Mg, 0.6% Fe	" " at 500°, "
5	5% Cu, 0.2% Fe	" " " "
6	3% Cu, 0.6% Fe	" " " "
7	3% Cu, 0.6% Fe	" " " " heat treated 130°
8	5% Cu, 0.2% Fe	" " " " " "
9	4 Cu, 0.5 Mg, 0.5 Mn, 0.6 Fe	Sand cast 720° heat treated 130°
10	" " " " " "	Forged, annealed 500°, quenched, aged
11	" " " " " "	" " " " heat treated 130°
12	4 Cu, 1.5 Mg, 2 Ni, 0.6 Fe	Sand cast, modified method (Archbutt's)
13	8% Cu, 0.7% Fe	" " at 700° C.
14	" " " " "	" " , modified way
15	" " " " "	Chill cast at 700° C.
16	" " " " "	" " , annealed 490°, quenched, heat treated 130°
17	12 Zn, 3 Cu, 0.7 Fe	Sand cast, 650° C.
18	" " " " "	Chill cast, 650° C.
19	" " " " "	" " 800°, annealed 480°, quenched
20	" " " " "	" " " " heat treated 130°
21	10.5 Si, 0.2 Fe	Sand cast, non-modified
22	10.5 Si, 0.2 Fe	" " sodium treated
23	10.5 Si, 0.5 Fe	" " " "
24	12 Cu, 2 Mn, 0.7 Fe	" " modified method

LIST OF SAMPLES ILLUSTRATING CORROSION EFFECTS OF 50% ACETIC ACID AT 80° (24 H.)  
Plate E

1	12 Zn, 3 Cu, 0.7 Fe	Sand cast, usual way	
2	" " " "	" " modified method	
3	" " " "	Chill cast at 800°	
4	" " " "	" " at 650°	
5	" " " "	" " at 800°, quenched from 480°	
6	" " " "	" " at 650°	" "
7	" " " "	" " at 800°	" " 480°, heat treated 130°
8	" " " "	" " at 650°	" " " "
9	12 Cu, 2 Mn	Sand cast, usual way	
10	" " "	" " modified way	
11	" " "	" " " "	
12	" " "	Chill cast, 700°	
13	Magnalite	Sand cast, usual way	
14	" "	" " modified way	
15	5% Cu	Forged; quenched from 500°	
16	" "	" " heat treated	

in anywhere from 20 minutes to 4 hours. The effects of nitric and acetic acid are shown for a 24-hour period.

The described test will yield in each case the following information:

1. The time required for the current to become minimum. It is inversely related to the ability of the sample to acquire a protective film.

2. The minimum current density shows the amount of electricity finding its way through weak spots in the film and indicates the amount of space occupied by secondary constituents.

3. The time which it takes the hydrochloric acid to start its attack is directly related to the strength and uniformity of the protective film.

4. The measured constant speed of corrosion in  $\text{cm}^3$  per  $\text{cm}^2$  of surface shows the characteristic corrodibility of the sample.

5. By weighing the sample after the test and calculating the factor of the loss in weight per volume of hydrogen developed, an indication is obtained of the chemical nature of the sample and its ability to withstand plain mechanical deterioration during corrosion. For instance, samples of an alloy containing substantial amounts of some compound or secondary element, precipitated within the individual grains by ageing or heat treatment, will lose more in weight than required by the amount of the total acid soluble components present. On the contrary, samples which have been homogenized by heat treatment and quenching will yield an almost theoretical factor.

6. By grinding down the surface of the specimens until all pits are removed and reweighing, the loss due to pitting is obtained, which feature is very important in judging the suitability of an alloy for various purposes.

Calling the time required for visible corrosion to start the factor  $A$  we set it equal to 100, for the best commercial aluminum. The characteristic velocity of attack by hydrochloric acid (or by any other acid) will be referred to as the

factor  $V$ . For the best grade aluminum metal it shall be taken as 1; the loss of weight per volume of hydrogen will always be given in mg per cc<sup>3</sup> and called  $C$ ; finally the loss due to pitting will be expressed as the percentage of the loss due to solution alone and will be called  $P$ .

#### THE ACTION OF SODIUM HYDROXIDE

Besides the accelerated corrosion tests using solutions of hydrochloric acid, some instructive results can be obtained from accelerated tests in solutions of sodium hydroxide of nearly the same molar concentration (the author used a 10% hydrochloric acid solution and a 11.5% solution of sodium hydroxide). This test does not yield even the slightest indication of the existence of a protective layer. It seems that the film of oxide is removed practically instantaneously and action starts immediately over the whole surface. Furthermore, while in the hydrochloric acid tests, the constant speed of attack does not become established until two or three, or sometimes four hours, have expired, with sodium hydroxide it becomes established after a few minutes and remains constant from this point on. The velocity of gas development is strictly constant, and the corrosion curve is a straight line practically from its inception.

A definite constant speed of corrosion by sodium hydroxide is also characteristic of all aluminum alloys. Wrought alloys containing only slight amounts of copper, magnesium or zinc show practically the same corrosion velocities as the parent aluminum metal. Wrought alloys which have been subjected to some kind of ageing either at room temperature or artificially by heat treatment, always show a markedly higher velocity of corrosion, which, however, remains at the same order of magnitude. Samples of casting alloys, prepared under conditions approaching equilibrium, form a class by themselves. Alloy "N° 12" with 8% copper, silumin and the German alloy, when cast under good conditions, will show almost identical speeds of corrosion. On the other hand, cast alloys obtained under conditions far from equilibrium or those con-

taining much magnesium, show a far higher velocity of corrosion. The results of repeated experiments with sodium hydroxide are usually quite identical.

TABLE XII  
THE ACTION OF 11.5% NaOH AT 24° C.

<i>Metal</i>	<i>State</i>	<i>Velocity of hydrogen development c.c./min./m<sup>2</sup></i>	<i>Mgs. loss per 1 c.c. of hydrogen</i>
Alloy 99.7	Annealed	24	72
5 Cu, 0.2 Fe	Rolled, quenched 500°	23	765
5 Cu, 0.2 Fe	Heat treated 130°	28	765
Duralumin	Sand cast, modified way	63	72
12 Cu, 2 Mn	Sand cast, ordinary way	36	74
8 Cu, 0.7 Fe	Sand cast, ordinary way	48	73
8 Cu, 0.7 Fe	Chill cast, quenched 500°	33	795
12 Zn, 3 Cu	Chill cast, modified way	33	80
10.5 Si	Sand cast, non-modified	32	75

#### CLASSIFICATION OF ALLOYS ACCORDING TO THEIR CORROSION RESISTANCE

It is general experience that wrought aluminum containing about 0.7% Fe shows a marked increase in corrodibility in comparison with 99.8% aluminum in practically any test. In fact, there is practically no reason at all why any wrought alloy should be better than pure aluminum. Only alloys containing copper show a definite increase in corrosion resistance in a few particular cases, and even then the beneficial action of copper has not been proven. On the contrary it has, for instance, been definitely shown that aluminum conductor wire containing 3% copper and subjected to the influence of atmospheric agents, corrodes rather quickly and becomes unfit for use after a few years.

As explained at a previous point the impossibility of obtaining pure aluminum in a mechanically reliable state makes

it necessary to use additions acting as grain growth and anneal inhibitors. Strains produced in a rolled or drawn piece of aluminum by cold work will eliminate themselves much more completely in pure aluminum than in metal where the shifting of the grains is obstructed by intergranular constituents. Opinions are divided as to which additions are the least deleterious for the chemical resistivity of aluminum, but it seems to be practically established that manganese is the best among them, with nickel and chromium following. Experience shows that hard aluminum containing about 1.5% manganese is actually a very good material as far as its ability to form a protective film and its low intrinsic corrosion velocity are concerned. It is second only to the regular commercial aluminum of the second grade, but is undoubtedly much stronger.

#### HARADA'S EXPERIMENTS

The Japanese scientist did not find manganese aluminum alloys any better chemically than plain aluminum and usually far less resistant than alloys containing copper or nickel. In fact, he deemed it possible on the basis of his results to develop a new alloy containing 2% copper, 1.5% nickel, and 1% iron to which he gave the name "Halumin," and for which he claimed a marked general increase in resistance to corrosion.

Alloys amenable to heat treatment, like duralumin, aludur and lantal are somewhat more corrodible than alloys containing manganese or copper only. The last two named occupy an intermediate position between hard aluminum (1.5% manganese) and duralumin. The aludur alloy, or its American cousin the 51-S, comes very near to hard aluminum in its corrosion resistivity. Higher amounts of magnesium than those used in aludur or duralumin tend to make the alloy less corrosion resistant, but an alloy with 5% magnesium shows still a notable resistivity to hydrochloric, nitric and acetic acids when used in a fully annealed and quenched state. After a further hardening heat treatment, at a low temperature, it becomes much more liable to corrode.



TABLE XIII. — COMPARATIVE CORRODIBILITY OF SOME MOST FREQUENTLY USED WROUGHT ALUMINUM ALLOYS

(LOSS IN GRS./M<sup>2</sup>/DAY)

Attacking Medium	Concentration %	Temp. °C.	Metal and Composition			
			99.8% Aluminum	3.0% Cu and 0.6% Fe	2.0% Mn and 0.7% Fe	Duralumin (4 Cu, .5 Mg, .5 Mn, .7 Fe)
Nitric Acid	67	24°	0.5	10.5	3.7	12.8
	67	80°	370 <sup>1</sup>	1065 <sup>3</sup>	740 <sup>5</sup>	1560 <sup>7</sup>
	45	24°	12.5	40.8	33.3	49.5
	23	24°	16.6	32.0	24.5	62.0
	23	80°	1160 <sup>2</sup>	3740 <sup>4</sup>	2070 <sup>6</sup>	3000 <sup>8</sup>
Acetic acid	50	24°	1	0.32	0.32	1.00
	50	80°	12	25.0	16.5	24.0
Sulfuric acid	15	24°	10	25.0	10.0	28.0

Remarks: <sup>1</sup> Little pitting; <sup>2</sup> Edges perpendicular to rolling badly pitted; <sup>3</sup> and <sup>4</sup> Pitting uniform, honey comb type; <sup>5</sup> and <sup>6</sup> Pitting concentrated at the diagonals of the cross section; <sup>7</sup> Surface almost clean, edges badly pitted; <sup>8</sup> Selective corrosion very deep in spots.

## CORROSION RESISTANCE OF WROUGHT AND CAST ALLOYS

The compositions of cast alloys cover a very wide range, which, taken together with the different condition of casting, affect the chemical resistivity to a great extent. For each alloy the corrosion resistivity in the cast state depends upon the method of casting (wet sand, dry sand or chills). The pouring temperature and subsequent heat treatment either increase the chemical homogeneity by homogenizing the alloy or decrease it by throwing certain compounds out of solid solution into a state of ultramicroscopic or fine microscopic dispersion.

No definite statement can be made concerning the influence of the method of casting and the temperature of pouring. Both may have opposite effects for different compositions. On the contrary, it is an absolute fact that a homogenizing heat treatment (followed by quenching) always increases the corrosion resistance, while an artificial hardening always decreases it.

Among cast alloys a line must be drawn between the chill- and the sand-cast state. While a definite rule cannot be laid down as to the influence of the method of casting, the author has made the following observations. In alloys where the ranges of solid solubility are negligible, for instance aluminum silicons, chill casting produces not only mechanically stronger, but also more corrosion resistant materials. However, the difference between the chill-cast and the sand-cast state is not so conspicuous in this case. The influence of contaminations is much more important. The sodium treatment used to modify and refine these alloys increases the chemical resistivity to some extent.

Casting alloys low in additional components, as, for instance, the U. S. Navy alloy with 2% copper and 1.5% manganese, the magnalite or "Y" alloy and various compositions of the duralumin type, when used for casting resemble the aluminum silicon alloys. Their ability to form a protective film, however, is much less marked, and their characteristic corrosion velocity much higher than that of the first group. In this case chill-cast alloys are definitely less corrosion resistant than sand-cast ones. The conditions are reversed when the alloys are subjected to the homogenizing heat treatment in the process of improving their properties. Chill-cast samples treated for some time at 500° and quenched show far more corrosion resistance than either the quenched or raw sand-cast samples. Finally, age hardening, whether natural or artificial (by heat treatment), once more lowers the resistivity of corrosion.

Alloys of the usual foundry practice, as, for instance, the American alloy usually called N° 12, and containing 8% copper, show much less corrosion resistance than the Navy alloy or magnalite. Here chill casting results in a higher strength, but a much higher corrodibility than sand casting. With the German alloy (12% zinc, 3% copper) conditions are reversed. The alloy is much less corrodible when chill cast and the difference runs into many hundred per cent. Chill casting of this alloy can be further improved both mechanically and chemi-

cally by heat treatment at  $450^{\circ}$  and quenching. In this state, it is very resistant, better than raw cast magnalite or the Navy alloy. Finally, the same alloy as chill or sand cast, heat treated, quenched and subjected to an artificial ageing, loses its chemical resistivity almost entirely. The characteristic velocity of attack by hydrochloric acid becomes rather high.

(Compare also figures 1-8, plate E.)

A large amount of work has still to be done in order to attain definite and substantiated ideas concerning the chemical resistivity of various aluminum alloys. Even the subject of pure aluminum has so far been treated in the most rudimentary fashion. The author has endeavored, however, to supply in the following a few figures giving a rough idea as to the resistivity of the various alloys to nitric and acetic acids plus their characteristic corrosion velocities for 10% hydrochloric acid and 11.5% sodium hydroxide solution.

#### Hard Aluminum (1.5-2% manganese plus .2 to .7% iron)

This alloy has been found by many investigators to be one of the least corrodible aluminum alloys to be used for general purposes. Its actual corrosion resistance depends largely on the amount of iron present and also upon the way in which the alloy has been manufactured. If cast from a high temperature, manganese aluminide will accumulate toward the center of the ingot and will be particularly dense along the diagonals of the rectangular or hexagonal cross section. Forging or rolling does not change the relative location of this accumulated manganese aluminide and the old diagonals form spots of chemical weakness in the finished alloy. Surfaces taken across the rolling direction or parallel with it but in the vertical plane will always be chemically weaker, and show noticeable pitting between the fiber layers exposed. The resistivity factors for this alloy will be:

A = from 25-45

V = 0.8-1.5

C = 0.75

P = 45-200%

The safety factor of 3 at least must be used for this grade in calculating the thickness of various parts.

All the figures mentioned above are understood to relate to the soft state, with all strains removed. Hard rolled alloys will possess the lowest A, a much higher V and a P up to 400%.

In 23% nitric acid at 24° C. the loss by dissolution will amount to 40 g. per m<sup>2</sup>/ day and the loss by pitting to 35%. The loss in a 50% acetic acid at 80° C. amounts to 15 g.

#### Aluminum Copper Alloys

Alloys containing around, but no more than 3% copper and 0.6% iron (made of medium grade aluminum ingot) will show

$$\begin{aligned} A &= 10-20 \\ V &= 1.3-5.0 \\ C &= 0.69-0.81 \\ P &= \text{up to } 175\% \end{aligned}$$

Annealing at 500° C. or thereabouts followed by quenching leads to the higher figures of corrosion resistance while a subsequent heat treatment of 130° increases the corrodibility.

Alloys containing 5% copper and 0.2% iron only will show:

$$\begin{aligned} A &= 8-20 \\ V &= 2.2 \\ C &= 0.73 \\ P &= \text{up to } 210\% \end{aligned}$$

Annealing at 500° C. and quenching leads to a higher chemical resistivity in this case. Heat hardening if carried out below 130° C. does not, however, greatly affect the above values.

A 23% nitric acid will dissolve from 50 to 80 grs. per m<sup>2</sup>/ day with a pitting up to 150% for the alloy containing 3% Cu and 0.6% Fe. Heat hardening produces an increase in corrodibility.

Sulphuric acid (15%) at 24° will dissolve from 25 to 50 grs.; the quenched state is the more resistant.

A 50% acetic acid dissolves about 20 grs. per m<sup>2</sup>/ day at 80°, the state of the metal making very little difference.

The 5% alloy shows nearly the same corrodibility in nitric acid (58–70 grs. /m<sup>2</sup>/ day), but less corrodibility in sulphuric acid (20 grs.) and about 25 grs. in 50% acetic acid at 80°. In the absence of iron, there is very little difference between the quenched (soft) and the heat treated (hard) state.

#### Aluminum Magnesium Alloys

An alloy containing 5% magnesium and 0.5% iron showed:

A = from 6 to 20

V = very variable and up to 5.4

C = from 0.78 to 1.0

P = from 100 to 150%

The quenched state (from 500°) makes definitely for more resistance. In this case the velocity of attack by hydrochloric acid may drop to nearly 1.

This alloy shows very little resistance to nitric acid, which has an attacking effect of from 420 to 450 grs. per m<sup>2</sup> per day, with about 125% pitting, the state of the metal making very little difference. In hot acetic acid (50% and 80°) the corrodibility is 40 to 48 grs.

#### Duralumin

Duralumin if made from medium grade aluminum containing about 0.5 to 0.6% iron, shows a very small value of A = 7–8 in the wrought (6–7 in the cast) state. V amounts to 3.8 for the aged and to 7.0 for the artificially hardened (130°) alloy. C = 0.80–0.90, P = up to 225%. The artificially hardened alloy is less resistant in all respects, provided the hardening has been carried to the maximum. While the relative pitting is lower for the artificially produced hard state, its actual magnitude is much higher. Otherwise duralumin shows:

62-82 grs. / m <sup>2</sup> / day	
( + 100% pitting)	in 23% nitric acid at 24°
28 grs.	in 15% sulfuric " " "
21-28 grs.	in 50% acetic " " 80°

The same duralumin composition (4.0% Cu, 0.5% Mn, 0.5% Mg, 0.0% Fe) if sand cast, will show

$$\begin{aligned} A &= 6-7 \\ V &= 11-16 \\ C &= 0.75-0.98 \\ P &= \text{about } 100\% \end{aligned}$$

When cast in the modified way suggested by Archbutt it combines a greater strength and soundness with a much higher corrodibility.

$$\begin{aligned} A &= 10-14 \\ V &= 2.5-3/8 \\ C &= 0.76-0.91 \\ P &= \text{up to } 260\% \end{aligned}$$

**Magnalite (4% Cu, 1.5 Mg, 2.0 Ni, 0.6% Fe)**

Casting in the modified way also produces a higher corrodibility. Chill casting increases the corrodibility in all respects, except pitting. V in this case = 4.6, for the alloy homogenized by quenching from 500°C. and is probably much higher in the raw state.

Nitric acid dissolves from 180-360 grs. / m<sup>2</sup> day with nearly 100% pitting. Acetic acid takes from 16 to 26 grs. / m<sup>2</sup> day, and the higher corrodibility relates to the sounder and stronger metal cast in the modified way.

**Alloy N° 12 (8.0 Cu, 0.7 Fe)**

$$\begin{aligned} A &= \text{from } 2.5-14 \\ V &= \text{from } 4 \text{ to } 5 \\ C &= 0.70 \text{ to } 0.78 \\ P &= 50 \text{ to } 100\% \end{aligned}$$

The modified method of casting produces a more corrosion-resistant alloy. The same alloy in 23% nitric acid at 24° will lose 470 grs. with 115% pitting and from 19 to 23 grs. in

50% acetic acid at 80°. In the last two cases the method of casting has hardly any influence.

Same alloy if chill cast shows

$$\begin{array}{l} A = 3 \\ V = 9.6 \\ C = .74 \text{ to } .89 \\ P = \text{up to } 70\% \end{array} \left. \vphantom{\begin{array}{l} A \\ V \\ C \\ P \end{array}} \right\} \text{increased corrodibility}$$

A homogenizing treatment at 500° followed by quenching improves the chill cast alloy slightly, while a subsequent heat hardening robs it of all chemical resistivity. A becomes practically equal to 0 and V --- 16.

In nitric acid the relations are practically the same, the chill-cast alloy showing 990 grs. per m<sup>2</sup>/ day loss in the raw state, and 850 grs. as quenched from 480° C. In acetic acid the alloy loses from 19 to 42 grs. and neither the method of casting nor homogenization by heat treatment changes the situation. On the contrary, hardening by heat treatment has a strong influence, resulting in an increased corrosion.

The effects of sulphuric acid upon this alloy are much less pronounced. It loses only 40 grs. per m<sup>2</sup> per day at 24° in a 50% acid against 8 for the purest aluminum.

A further increase in the amount of copper present in the alloy continuously decreases its corrosion resistance and with a content of 12% Cu, 2% Mn and 0.7% Fe one obtains:

$$\begin{array}{l} A = 1-3 \\ V = 7.4-20 \\ C = 0.78-1.14 \\ P = \text{up to } 75\% \end{array}$$

Casting in the modified way at a lower temperature also produces a higher corrodibility in spite of the increased soundness.

The losses in nitric and acetic acids for this alloy are comparable with those of alloy N° 12.

#### Silumin (10.5% Si plus 0.2-0.7% Fe)

This alloy if well treated and made of the best grade of aluminum shows a rather high corrosion resistance in spite of

the fact that due to the large amount of elementary silicon present, the protective action of the oxide film is not high. For the best castings in the modified state:

$$\begin{aligned} A &= 5 \\ V &= 1.9 \\ C &= 0.88 \\ P &= 95\% \end{aligned}$$

If not modified by sodium treatment, V increases to 3.5 and P to 200%.

In 23% nitric acid at 24° C. the purest type of alloy loses from 93 to 105 g. with a pitting loss of 100%. Its loss in 15% sulphuric acid equals 21 g. and in 50% acetic at 80° from 10 to 20 grs.

The presence of as little as 0.4% of iron lowers A to 3, raising V to 8.5 and P to 145%, C remaining unchanged. In nitric acid this contaminated silumin or alpax will lose from 180 to 220 g. and in acetic acid nearly 28 grs. A further increase in iron increases corrodibility, but to a lesser extent than soundness and strength.

#### German Alloy (12% Zn, 3% Cu, 0.7% Fe)

Sand castings made of this alloy are particularly weak in their corrosion resistance. A does not exceed 2, V = 20-25, C = 0.87 to 0.89 and P up to 100%, the method of casting having very little effect. In 23% nitric acid the loss is from 275 to 350 g. by solution and the sample shows enormous amount of pitting. The loss in 50% acetic acid at 80° amounts to 47 g.

Chill casting materially decreases the corrodibility, particularly if done from the comparatively high temperature of 800°. The characteristics become:

$$\begin{aligned} A &= 8 \\ V &= 2-7.4 \\ C &= 0.76 \\ P &= 70\% \end{aligned}$$

In nitric and acetic acids, chill-cast alloys show the same behavior as the sand cast ones.



Chill castings homogenized by heat treatment at  $450^{\circ}$  and quenching show a great improvement:

$$\begin{aligned} A &= 25-40 \\ V &= 2.0-5.0 \\ P &= 100\% \end{aligned}$$

In nitric acid the homogenized chill castings lose about 80 g. with 120% pitting. In acetic acid at  $80^{\circ}$  they lose from 25 to 30 g. Sulphuric acid (15%) at  $24^{\circ}$  dissolves about 30 g. Subsequent heat treatment at  $130^{\circ}$  greatly increases corrodibility, though it does not improve much the hardness and strength. In this state one obtains

$$\begin{aligned} A &= 5 \\ V &= 18-50 \\ P &= \text{at least } 350\% \end{aligned}$$

In nitric acid the loss becomes nearly 190 g. against 50 g. in the quenched state and in acetic acid it increases to 40 g.

#### ACTION OF DIFFERENT REAGENTS UPON ALUMINUM ALLOYS

Approaching the subject from the standpoint of the corroding media instead of from the different alloy compositions the following situation is found:

Hydrochloric acid of all moderate concentrations is practically the strongest solvent for aluminum provided its surface is exposed. Starting from 5% hydrochloric acid and upwards, there is no reagent of the same molar concentration which can develop a velocity of attack even nearly as great as that of hydrochloric acid.

Hydrofluoric acid in moderate concentrations is the next potent corroding medium for aluminum alloys.

Solutions of sodium hydroxide and potassium hydroxide follow with an almost equal velocity of corrosion.

Sulphuric acid of moderate concentrations falls far below the reagents mentioned. In fact, the action of an acid of a concentration from between 15 to 30% upon aluminum and

its alloys, particularly upon those containing copper in solid solution is very small, even lower than that of 23% nitric acid. It may be said that vessels made of aluminum metal or of an aluminum copper alloy with not over 2% copper can be safely used for transportation and storing of sulphuric acid of these concentrations at low temperatures, provided the slight contamination of the acid with aluminum sulfate is of no consequence.

Nitric acid of moderate and particularly of high concentrations is still less corrosive to aluminum than sulphuric acid. Next to nitric, and appreciably less corrosive, are acetic acid

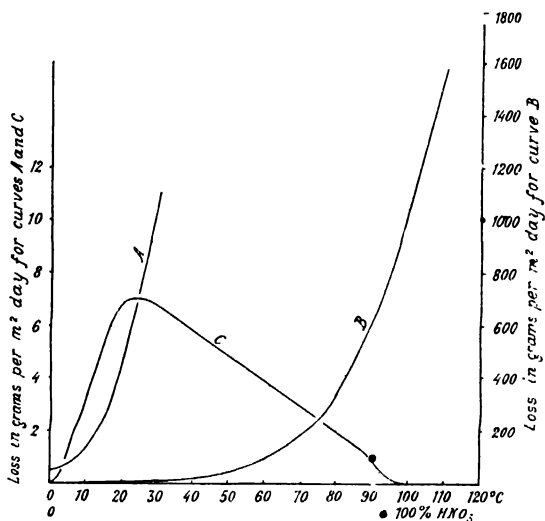


FIG. 85. Influence of temperature (curves A and B) and of concentration (curve C) upon the corrosion of aluminum in nitric acid.

and certain organic acids of the fatty series. Their action upon aluminum even in the boiling state is not very strong and vessels made of aluminum can be safely used in industries handling these chemicals. A few scattered observations by Seligman seem to show that the fully dehydrated fatty acids possess a highly corrosive action upon aluminum. Seligman's experiments were not, however, extensive enough to be con-

clusive, and besides, these fully dehydrated acids are practically unknown to the industry.

The influence of temperature and concentration of the corroding medium upon the velocity of corrosion are rather important factors, but so far, not much investigation has been done in this direction. Data are available, however, concerning the influence of the concentration of nitric and acetic acid

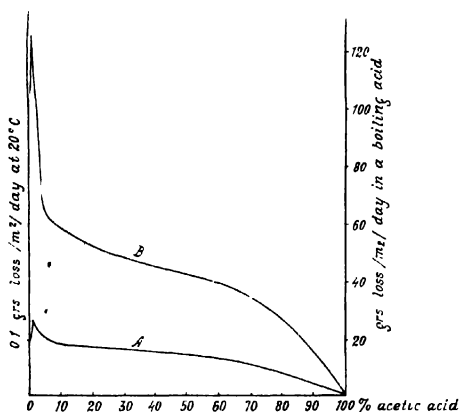


FIG. 86 Influence of concentration upon the corrosion of aluminum in acetic acid

upon the best aluminum metal at normal temperatures, and for the latter one at the boiling point also. For the usual commercial nitric acid of 1.42 sp. gr. (67% by weight) the influence of temperature up to 120° is known. These data were reproduced in Table VII and are presented now in Figs. 85 and 86.

#### ACTION OF ACID SOLUTIONS OF LOW CONCENTRATION

In this case the condition changes greatly, almost all inorganic acids in concentrations below 1% affecting aluminum in nearly the same manner. Nitric acid is practically the worst of all, although hydrochloric is almost identical in its action. It is necessary to add on this occasion, that the experiments so far accomplished with solutions of low concen-

tration have been neither systematic nor of sufficient duration to produce definite results.

#### ACTION OF SALINE SOLUTIONS

The majority of salts soluble in water are detrimental to aluminum and corrode it to various extents. The mechanism of their corrosive action is not exactly understood so far. There is practically no known reason why common salt—sodium chloride—should corrode aluminum. The most logical explanation is based upon the basis of peptization. A number of salts have a definite peptizing action upon the protective film, and salts containing the anions of the halogens are the worst of all. The action of these anions may be either increased or decreased by the cation. Sodium, for instance, adds to the action of the chlorine-ion more than potassium, and ammonium more than sodium. Salts containing calcium or magnesium are still more active as corroding media, inasmuch as they are somewhat hydrolyzed in aqueous solutions, which then contain a certain amount of free acids.

It has been impossible so far to predict the peptizing action of various salts in aqueous solutions upon the protective film formed on aluminum and its alloys. It is known, however, that carbonates are less harmful than chlorides and that nitrates, bichromates and permanganates, all definite oxidizers, stop the peptizing action and help the protective film to keep intact. This protective action is so definite that in many cases where the corroding agent is not too strong, an addition of traces of a bichromate or nitrate will prolong the life of the aluminum article subjected to the corroding influence. However, there is no reason so far to expect that bichromates or nitrates will exert their film protecting action even in the presence of the stronger acids (hydrochloric, hydrofluoric).

On the other hand, this protective action disappears entirely in solutions of sodium hydroxide and potassium hydroxide. In fact, it seems that the corrosion of aluminum in these reagents requires a preliminary formation of a film of oxide.

In a paper by L. Callendar (*J. Inst. Met.*, 1925, part 2), the author sets forth the results of his work on the peptization and passification of various saline solutions. The method consisted in comparing the voltages and currents produced when aluminum alloys of approximately the same type were immersed together as two electrodes in a solution of a given salt, one of the electrodes being covered by a protective film. The results of these experiments are not yet amenable to a practical interpretation, but point to a certain path for future investigations.

#### ACCELERATED TESTS FOR LONG LASTING SLOW TYPES OF CORROSION

Corrosion by saline solutions, although rather slow, sometimes results in the failure of aluminum-made articles due to the localized action and consequent weakening of the article if it be subjected to strains. This is particularly true for parts of gas engines and structural parts of seagoing craft, airplanes and dirigibles. Here corrosion testing is also in its beginning and the results obtained so far are not very conclusive. Without reviewing the few experimental data obtained so far, let us pause only at the very interesting method for testing the resistance to saline solutions by the peroxide-sodium chloride method, also proposed by Mylius (*Z. Met.*, 1925, v. 17, p. 14). Taking into consideration the fact that corrosion by sea water is usually a combination of oxidation by the active oxygen dissolved in the water and the peptizing action of sodium chloride, and other salts, Mylius devised an accelerated test in which a solution of common salt is activated by a certain amount of hydrogen peroxide. In this test a sample of standard area is submerged in a solution of sodium chloride of a standard volume and concentration. A definite amount of hydrogen peroxide is previously added to this solution and this concentration is subsequently maintained by small additions. After 24 hours the oxide accumulated in the bottom of the test tube is determined by ignition and weighing. This

test permits a study of the corrosion resistance of a given sample of metal to sea water under variable conditions, for instance, with the protective film fully removed by a previous treatment with sodium hydroxide, or with one covered with the primary film (as formed in the rolling process or obtained in some artificial way). Unfortunately, Mylius himself tested samples of wrought aluminum only, and no conclusions may be drawn as to the suitability of his test to other alloys.

On this occasion the experiments by Zimmerman of the U. S. Air Service (J. Eng. Ind. Ch., 1925, v. 17, p. 359) ought to be mentioned. He studied the corrodibility of various cast alloys by distilled water, atmosphericals<sup>1</sup> and the salt spray. In each case, the regular alloy N° 12 made of second grade aluminum, and containing about 1% iron showed the highest corrodibility. A decrease in the amount of iron was found much more advantageous than a decrease in the amount of copper. Alloys containing substantial amounts of silicon showed the least corrodibility by the three agents studied. Zimmerman's data were too scattered and incomplete to enable one to judge the general resistivity of various casting alloys to the slow types of corrosion.

<sup>1</sup> By "atmosphericals" are meant clean and polluted air, also rain and snow.



## **PART V**

### **ALUMINUM ALLOYS IN ENGINEERING WORK**





## ALUMINUM ALLOYS IN ENGINEERING WORK

### INTRODUCTION

ALUMINUM and its numerous alloys present a rather wide field for a selection of various combinations of mechanical features. From plain cast aluminum with a tensile strength of not over 10,000 lbs. per sq. in. and practically no rigidity at all, through a number of intermediate alloys, one arrives at certain compositions possessing in the wrought, heat treated and cold rolled (or drawn) state, strengths up to 80,000 lbs. per sq. in. and elastic limits up to 45,000 lbs. By grouping all requirements as to strength, wear resistance and cost of production an alloy best suited for any given purpose may be selected.

Strength, cost of production and wear resistance are not, however, the only features which indicate the fitness of an aluminum article for a given purpose. The qualities known as endurance, resistance to corrosion and impact resistance must be considered in many instances. The property of fatigue resistance or endurance implies the ability of a given alloy to withstand a certain maximum stress when this stress is subject to a practically indefinite number of reversals (from 10 to 100 millions according to the standards of various authorities). Running fatigue tests with hundreds of millions of reversals is, however, tedious, and according to the latest data, the endurance values may be estimated quite accurately from the proportionality limit in tension (85% of the latter). The fatigue limit is usually only slightly lower than the proportionality limit provided the metal has not been cold worked after normalization. In cases, however, where the metal was worked cold only a small part of the additional static rigidity is found in the endurance limit and the latter has to be determined by direct fatigue tests. In normalized alloys, however, the en-

durance factor follows the elastic limit and does not represent an independent feature.

Unfortunately, in the search for materials of high strength and high endurance, two other properties, namely, resistance to impact and to corrosion, often escape the attention of designers and metallurgists. Thus, the fact is frequently overlooked that aluminum alloys of the highest strength are rather weak in resistance to shocks. For example, it should be noted that, while a very strong alloy of the duralumin type has an Izod value at 20 ft. lbs. immediately after quenching, this may drop during ageing to something like 3 or 4 ft. lbs. A number of alloys much weaker than duralumin in direct tension will show a higher impact resistance.

#### LOW IMPACT STRENGTH OF DURALUMIN TYPE ALLOYS

This lack of agreement between impact resistance and tensile strength must be taken into consideration, and it must be remembered that within the wide range of aluminum alloys there can be found many with good tensile strength and high impact resistance. Aludur and also "51S," *i.e.*, the aged or artificially hardened wrought alloys containing magnesium, and substantial amounts of silicon but no copper, will show only about 20% less strength than duralumin with a much higher impact strength (at least 9 ft. lbs.). Both the German "Lautal" (4% copper, 2% silicon) and the American "25S," which require a heat treatment to harden, permit, if suitably manufactured, a close control of the heat hardening process. The conditions may be so controlled as to obtain only a slightly lower strength than the maximum possible, securing simultaneously a fair impact resistance. Even the plain 4.5% copper alloy for example may be heat hardened so as to secure a Brinell hardness of 90 and a strength of 50,000 lbs. with an Izod value of 10 ft. lbs. against its possible maxima of 130 Brinell and 58,000 lbs. tensile strength but only 2.5 ft. lbs. Izod.

## LOCAL CORROSION

Too frequently a sensitivity to local corrosion will counteract the high strength of an alloy. True, we have not yet reached a definite conclusion concerning the factors governing the corrosion resistance in alloys of the duralumin type. We do know, however, that localized action is almost entirely overcome in wrought alloys made of the purest aluminum ingot and containing only small amounts of manganese (up to 1%) and small amounts of copper (not above 2.0%). It is probable, therefore, that frequently a substitution of the easily workable aluminum-manganese-copper alloy for one of the duralumin type, with a suitable change in the shape and dimensions of the part to be manufactured, will result in a greater safety and lower costs.

## HOW TO CHOOSE A DURALUMIN COMPOSITION

Should, however, the plain wrought alloys be found unsuitable for a given purpose there still remains a broad field of choice among the heat treatable alloys, provided a maximum strength in tension is not made a fetish. The fact must be emphasized that in no industrial or structural application will a part made of an aluminum alloy fail in pure tension. All parts subject to tension alone must be made of some high grade steel wire, particularly of a non-rusting type with an ultimate strength of about 200,000 lbs. and an endurance limit above 60,000 lbs. The actual weight of such parts will be quite below those made of duralumin.

Nor does a duralumin part fail due to its incidentally low endurance limit. It seems to be established that even fine scratches upon the surface of a sample subjected to the fatigue test will lower the characteristic endurance limit considerably. A corrosion pit or ditch may prove just as detrimental as a scratch if not worse.

Granted, however, that a maximum tensile strength is not a predominating requirement, one arrives at the conclusion that most of the present-day duralumin compositions are un-

duly overloaded with additional elements. Some manufacturers do it unconsciously, striving for higher strengths or lower costs; others run into it in going around somebody's patent rights.

#### THE FUNCTION OF COPPER IN DURALUMIN

The engineer who intends to use duralumin in his work must clearly understand the value of, and the part played by, various additions. He must know, for example, that a small amount of copper is required for three reasons, namely: (1) to make the alloy stronger by virtue of the copper entering into solid solution, *i.e.*, substituting for a certain amount of atoms of aluminum; (2) to make it more noble chemically, and (3) to accelerate the precipitation of the "keys" or hardening crystals of magnesium silicide.

On the other hand an excess of copper may lead to a local electrolytic action along the grain boundaries provided it crystallizes there as copper aluminide (particularly if, due to a too high temperature of heat treatment, the latter melts and solidifies during quenching in the form of "filigrees"). More frequently it accelerates the intracrystalline corrosion due to the precipitation of the excess copper aluminide from the solid solution during the ageing or artificial hardening. Finally it leads also to an excessive stiffening of the grains and their boundary cement, which leads to a low impact resistance.

#### THE FUNCTION OF MAGNESIUM

Of the other elements, magnesium has only one definitely advantageous function, *i.e.*, the ability to form the silicide,  $MgSi$ , of a variable solubility in solid aluminum and with a definite tendency to form an ultramicroscopic precipitate reinforcing the grains in the age-hardening state. For this purpose it must be made certain that the amount of silicon present is fully sufficient to bind all the magnesium added to the alloy. It must be said that hardly any care is being taken at the present time to produce alloys in accordance with this strictly logical requirement. Too frequently the amount of silicon

present cannot bind more than 0.35% of magnesium, while anywhere from 0.5 to 1.5% Mg is present.

Excess of magnesium will prove harmful in an alloy of the duralumin type. In the first place magnesium is a definite oxygen carrier, and while alloys containing little or no magnesium may be heat treated (prior to quenching), in any gas or coal fired furnace with no protecting medium, those high in magnesium and low in silicon must be protected by a bath of fused salts (nitrate + nitrite of sodium). In a high magnesium alloy the magnesium silicide formed is practically insoluble at all temperatures and will be found at the grain boundaries. Here it does not develop much of a strengthening effect (far less than copper aluminide), due to its brittleness, and is easily corroded, leaving intergranular pits. On the contrary magnesium silicide, precipitated within the grains during the ageing process, is nearly the least harmful of all components of an aluminum alloy. It has practically no accelerating action upon the intracrystalline corrosion of the alloys. This explains why Aludur (or "51S") ranks next to commercial aluminum in corrosion resistance.

#### PREVENTION OF GRAIN GROWTH

Besides copper and magnesium whose functions we have discussed before there are additional elements whose main positive action consists in the prevention of grain growth. An alloy containing only copper or magnesium silicide or even both together will show, if nothing else is present, an enormous grain growth during the long period of the treatment at 500°, required to homogenize the alloy and bring the maximum amount of Cu and  $Mg_2Si$  into solid solution. Only such additions as will stay undissolved and evenly distributed along the grain boundaries at this temperature can prevent their growth by plain mechanical obstruction.

It remains to discuss the nature and amount of this third type addition required to insure the grain growth prevention with the least deleterious effect upon ductility and corrosion resistance in particular. The importance of this requirement

is evident. Practically every aluminide of a heavy metal will be more electrochemically noble than aluminum and so will lead to local electric currents at the grain boundaries. The smaller the amount of the particles of aluminide and the less noble they are the less electrochemical action will ensue.

As explained in the chapter on the corrosion of aluminum alloys, there is probably no aluminide with less potential difference against aluminum, than is displayed by manganese aluminide. This explains (though probably post factum) why manganese forms the usual third additional element entering into the structure of duralumin. Chromium is probably the second one in this respect among the accessible metals.

#### SILICON AND BERYLLIUM AS GRAIN GROWTH INHIBITORS

Silicon and beryllium are also apt to crystallize at the grain boundaries of the alloys and might therefore be used as grain growth inhibitors. In fact, "Lautal," with 4% Cu and 2% Si seems to constitute a product where this property of silicon is made use of. In the American "25S" alloy, silicon partakes in the grain growth preventive action together with manganese. Beryllium has not so far been used for this purpose, at least commercially.

There was so far a complete lack of information concerning the electrochemical differences between aluminum and silicon or beryllium. From the standpoint of plain corrosion there are two contradicting facts, one that high silicon alloys are better than any other casting alloys in their general resistance to corrosion and, second, that small amounts of silicon, so small in fact, that they may completely enter into solid solution in the wrought and annealed metal, are deleterious to the resistance of aluminum to dilute acids and various chemicals (Harada).

The author found recently that both silicon and beryllium must be rather close to aluminum in the electrochemical series,

the potential difference between aluminum and silicon being the least among the various couples. Beryllium is slightly more electropositive and silicon electronegative than aluminum.

At any rate, the conclusion must be that in the present state of our knowledge manganese and silicon are the only safe and nonexpensive grain growth inhibitors. In amounts from 0.5 to 1.0% the first one will form from 1.2 to 2.4% of aluminide of manganese and this is undoubtedly sufficient for the purpose mentioned.

This reasoning is not, however, usually applied in the manufacture of duralumin. While an alloy containing 2.0% copper, 0.6% Mg, 1.0% silicon (to insure the complete tying up of the magnesium) and 0.6% manganese will show, if properly manufactured, about 52,000 lbs. strength, and a possible maximum of chemical stability, there is a tendency to use not less than 3.5% copper. The aluminum ingot accepted in the manufacture contains usually about 0.6% iron.

#### OVERLOADING DURALUMIN ALLOYS

The additional 1.5–3.5% copper cannot fail to increase the intragranular corrodibility, while the iron, by forming nearly 1.4% of Fe Al<sub>3</sub>, located mostly at the grain boundaries, increases the intergranular corrosion; in fact, there is no doubt, that the difference of potentials between iron-aluminide and aluminum is nearly the largest obtainable under usual additions (see page 168).

Certain manufacturers add chromium, vanadium and very frequently nickel to their particular duralumin compositions. Chromium, as above mentioned, is probably the next after manganese as regards harmlessness, while nickel shows some secondary tendencies (forming a protective coating (film) of a deep blue color), which reduce the potential difference for the NiAl<sub>3</sub> compound. However, those who use Cr, V or Ni do not care to drop manganese completely.

As a consequence the alloy becomes overloaded with various constituents. This undermines the workability, lowers the



ductility of the final product and increases the chances of intergranular cracks and intergranular corrosion.

#### GENERAL SUGGESTIONS FOR THE SELECTION OF WROUGHT ALUMINUM ALLOYS

In conclusion it must be stated that the choice of aluminum alloys in the wrought condition might proceed along the following lines:

Parts where the highest rigidity is required, and corrosion is practically eliminated, may be made of a high loaded duralumin (5.3% Cu, 0.7% Mg, 0.5% Si, 0.8% Mn and 0.5–0.8% Fe, with or without small amounts of Ni, Va, Cr, etc.). The addition of Cr or Ni may be very beneficial in alloys having to stand temperatures of 200–230°.

Parts requiring good rigidity and particularly insurance against failures by fatigue or corrosion plus fatigue should be made of the *rational* duralumin alone (2.0% Cu, 0.5–0.7% Mg, 0.6% Mn and 1.0% Si).

Parts the shape of which may be so changed as to bring the main mass of the metal in the most economical position (I beams, tubular stays) should be made of an alloy with 2% Cu and nearly 1.0% Mn, and given a slight amount of cold work (for instance 10–20% area reduction) after the final anneal. This amount of cold work may not be eliminated by a spontaneous or low temperature anneal and will increase the rigidity (proportional and elastic limits) quite noticeably. The alloy, with not over 0.2% iron present, will be more reliable, less corrodible and less costly than any duralumin composition. Where corrosion is of little importance, as much as 0.7% iron may be allowed, and the amount of manganese can be reduced.

Where corrosion resistance is the main factor, only the purest aluminum sheet or tubing should be used. The metal may be reinforced in points out of contact with the corrosive medium by beams, ribs, etc., made of the 2% Cu, 1% Mn alloy (joined by welding) or of duralumin (joined by riveting).

TABLE XIV. — PROPERTIES OF A FEW ALUMINUM ALLOYS USED IN THE WROUGHT FORM

Alloy	Composition	State of the Metal	Brinell # 500/10	Shore # Mg. hammer	T.S. Lbs. Sq. in.	El. Lim. Lbs. Sq. in.	Endurance Limit $\sigma_t$ $10^8$ rev.	$I_{2nd}$ #
1st grade Al	0.3% imp.	fig 12, 500°, q		7	13000	3000	4500	15.0 (bent)
"Hard" Al	2% Mn, 0.6% Fe	fig 12, 500°, q	28	12	18000	6000	7500	20.0 (bent)
Al-Cu alloy	3% Cu, 0.7% Fe	fig 12, 500°, q	43	15	27000	12000		18.5 (bent)
Al-Cu alloy	3% Cu, 0.7% Fe	+5, 130°	50	10	36000	13000		16.0 (bent)
Al-Cu alloy	5% Cu, 0.2% Fe	fig 12, 500°, l	65	31	32000	13000		26.0 (broke)
Al-Cu alloy	5% Cu, 0.2% Fe	+5, 130°	90	40	52000	22000		14.0 (broke)
Lautal	4% Cu, 2% Si, 0.5% Fe	10, 130°	114		54000	23000		
Al-Mg alloy	5% Mg, 0.7% Fe	fig 12, 480°, q	40	17	38000	18000		6.0 (broke)
	5% Mg, 0.7% Fe	+5, 130°	54	25	42000	20000		2.3 (broke)
Duralumin	4.3% Cu, 0.6% Mn	commercial	114	50	61600	29800	21500	4.0 (broke)
	10.4% Mg, 0.5% Fe, 0.3% Si	as quenched	70	28				20.0 (broke)
		7h, 130°	120	35				2.5 (broke)
"51S"	0.55% Mg, 0.55% Fe,	commercial	0.2	38	43000	17500	12400	9.0 (broke)
"25S"	0.55% Si + 0.6% Cu, 0.8% Mn, 0.8% Si	commercial	110		59500	24200	16000	8.0 (broke)

fig. = forged; 12, 500°, q = quenched after 12 h at 500° C.  
 5; 130° = treated 5 hours at 130° C. after quenching.

## ALUMINUM ELECTRIC CONDUCTORS

A very important application of aluminum is found in its uses for electric transmission lines. Pure aluminum, with a conductivity of nearly 65% of that of pure copper, if used for overhead wires carries a constant gravity load of less than 30% of that carried by a copper, provided the span and the sag of the wire are identical. With 54,000 lbs. strength for hard drawn copper and 40,000 for hard drawn aluminum the safety factor will frequently be in favor of aluminum.

Aluminum suffers, however, much more from temperature variations than copper and is more likely to recrystallize under strain. The phenomenon of the metal slowly flowing down the span of the wire, and making its most heavily stressed parts grow thinner frequently happens with copper wire and is still more likely to happen within aluminum. Accordingly aluminum overhead wires will always call for a substantial reinforcement with steel wire cores unless the span is small enough to make the stress of the wire rather low.

One has to remember on the other hand, that in many cases the electric transmission engineer is compelled to give up pure copper and use alloys which show no more than 45% conductivity, provided they develop in the hard drawn state a strength of 75,000 lbs. and are free from the feature of the metal flow.

Among aluminum alloys there are such, which after heat treatment develop a very favorable strength with nearly the same conductivity, *i.e.*, 45% of that of copper.

Certain unexplained factors cause changes of electric conductivity in alloyed aluminum to proceed somewhat differently from those in other alloyed metals. Additions which do not enter into solid solution and should accordingly have little effect upon aluminum, act, on the contrary, in a rather pronounced and deleterious manner, iron and manganese being practically the worst elements in this respect per unit of weight. With these two absent, and with other additions so chosen as to inhibit each other from staying in solid solution, the alloy will show a high electric conductivity.

Here one arrives at aluminum alloys carrying well balanced amounts of silicon and magnesium plus small amounts of copper. Such alloys must be made of the highest grade of aluminum ingot, melted on a magnesite bottom of a large furnace, and carefully controlled before pouring, so as to contain 0.75% magnesium and 0.45% silicon plus 1.5% copper. In the finished, carefully heat treated state they possess a resistance of 3.65 microhms per cm<sup>2</sup> only. This relatively high conductivity is coupled with a strength of 42,000 pounds and a fatigue limit of 10,000 pounds at 10,000,000 reversals with no cold work being present. In the heat treated state these alloys do not become annealed below 130° C. and are safe against metal flow. Their specific weight still not exceeding 33% of that of a high conductivity bronze, the safety factor for a section of the same current-carrying capacity will be much better and the wire will permit a substantially longer span.

A good precaution against corrosion failures of either pure aluminum cables or those made of the alloy mentioned, consists of passing the wire through a solution of bichromate, nitrate, borate, etc., always having it connected to the - pole of an electric generator. A covering of oxide is produced and it prevents atmospheric corrosion for a considerable time.

### CASTING ALLOYS

In a number of cases wrought alloys are out of place for reasons of price, inferior machineability, too much friction, high wear or of a combination of a number of these properties. In consequence one has to resort to castings and to select the most suitable alloy for the given purpose.

Certain rational principles of choice can be applied in this case instead of the irrational one unfortunately most frequently used. At the present time, alloys of high strength are being sought for, to the neglect of other properties. The only secondary requirement is that of a slight ductility, be it even as low as 0.5-1.5% elongation in 2". The prevalent idea seems to be that any part will in the final account fail in ten-

TABLE XV. — ELECTRIC RESISTIVITY OF ALUMINUM ALLOYS

<i>Alloy</i>	<i>Composition</i>	<i>State of the metal</i>	<i>Resistivity</i> $\times 10^{-6}$ <i>microhms</i>	
1st grade aluminum	o 3% impurities	Annealed wire	2.65	Richards
2nd "	o 5% Fe, o 15% Si	"	3.13	Matsumoto
"	o 5% Fe, o 15% Si	Cast	3.54	"
"	o 5% Fe, o 15% Si	" and annealed	3.31	"
"Hard"	2% Mn, o 6% Fe	Annealed wire	4.90	Corson
Duralumin	4.3% Cu, o 4% Mg, o 5% Mn, o 9% Fe	"	3.79	Matsumoto
"	o 4% Si	Cast	5.79	"
"	5.3% Cu, 1.15% Mg, o 5% Mn, o 8% Fe	" annealed	4.42	"
"	Fe	Annealed wire	4.18	"
"	o.45% Si	Cast	6.07	"
"	68.1A <sup>1</sup>	" annealed	4.43	"
"	3.4% Cu, o 5% Mg, o 4% Mn, ? Fe	" 500° q-d	5.57	"
"	68.1C <sup>1</sup>	Annealed wire	3.70	Meissner
"	4.5% Cu, o 5% Mg, o 5% Mn, ? Fe	530° q-d	4.48	"
"	8% Zn, o 5% Mg, ? Fe	aged	5.00	"
"T" <sup>1</sup>		h. t. 200° C.	4.26	"
		Annealed wire	3.90	"
		530° q-d	4.48	"
		aged	4.85	"
		Annealed wire	4.00	"
		530° q-d	4.17	"
		aged	4.44	"
High Conductivity	2% Cu, 1% Mg, o 6% Si, o 2% Fe	h. t. wire	3.60	Corson

<sup>1</sup> German trademarks.

sion, and that in the more complicated case of external bending forces the distribution of internal stresses will follow the laws of statics developed for much more uniform materials.

This is not, however, the case. No aluminum casting fails in straight tension, be the latter constant or fluctuating. Most failures are due to shocks, the second largest number to bending and the remainder to shear.

The chances of failure in shear can easily be taken care of by a rather localized reinforcement. Those of bending and impact must be eliminated by a careful choice of composition and method of handling.

In a number of cases, low friction and good wear are the most important requirements. Gas engine cylinders and pistons are the best instances of this kind.

#### ALLOYS HIGH IN COPPER OR ANTIMONY

High wear resistance can only be obtained by the use of high copper or high antimony alloys. Only these two will form under suitable handling well distributed, reasonably large and more or less equiaxed particles of simple aluminides. Metals like iron, manganese or nickel if present in 2% or more, form very brittle, very hard and unevenly distributed needle-like crystals or chains of crystalline fragments. They crumble out, cut the surface in contact, and cause attrition.

However, cast alloys high in either copper or antimony (the latter is not so far much in use) also are not too ductile. Alloys with more than 10% Cu or 6% Sb may hardly show more than 0.7 ft. lbs. in the Izod test. The resistance of the alloy N° 12 to fracture in a slow bending test taken as a unit, an alloy with 10% Cu is not apt to register more than 0.6.

Both these features can be substantially improved by a suitable heat treatment. In fact one cannot recommend strongly enough the practice of returning the castings before the final machining to a furnace, where they may be kept at 480° C. for twelve to twenty hours followed by quenching in boiling water or cooling by a jet of cold air. This treatment

causes the excess copper aluminide (above 5%) and the larger part of all other aluminides present to coagulate, and so brings about an increase in wear resistance of the casting. It will also eliminate chemical inhomogeneity, corrodibility and thin down the intercrystalline cement. In consequence the Izod figure goes up to 1.5 ft. lbs. and the bend resistance increases by 100%.

#### SECONDARY ADDITIONS IN PISTON TYPE ALLOYS

It is customary to add to such alloys certain amounts of either iron or manganese, sometimes nickel. An addition of magnesium is also resorted to.

It is a fact, that the first three share the ability to make the alloys stronger at high temperatures, but it is somewhat doubtful if this feature is of much value in aluminum pistons. At any rate iron or nickel may be used with little hesitation in engines working on solid ground. For sea-going motors or airplanes, compelled to use an air carrying a mist of salt water, they may prove more detrimental than desirable. Manganese may be used advantageously for pistons subjected to heat treatment, but in the raw castings it acts for some unknown reason as the strongest heat conductivity reducing factor.

The use of small amounts of magnesium as recommended by some authors serves no rational purpose. In fact our aim ought to be to prevent as much as possible the slow heat treatment to which the quenched piston is subjected in its working conditions, and not to add something which will accelerate the hardening process. It is better to have a piston, whose material shows only 28,000 lbs. strength with 1.5 ft. lbs. Izod and 1.5% elongation than one with 38,000 lbs. but with 0.5 Izod and 0.5% elongation only.

#### CASTINGS OF THE CRANKCASE TYPE

In a number of cases the shape of the casting is very complicated and its walls must be as thin as possible at the same time. This makes low shrinkage the most important of all requirements while the uniformity of the casting will be the

next one to be considered. Rather frequently such castings (crankcases for instance) are made of the usual alloy N° 12, but this is not the most desirable solution of the problem. Much less shrinkage with a good machineability, and much more uniformity may be obtained from compositions which we call Dix alloys (3-5% Cu and 4-7% Si). These alloys with or without a small addition of magnesium will be substantially strong and ductile for the application described even in the raw state; if they are subjected in addition to a suitable heat treatment all their copper will go in solid solution and in consequence they will possess a greatly increased impact and bend resistance. It ought to be demanded, however, that the aluminum used to make these alloys should not contain more than 0.3% iron. Iron, which in the presence of silicon forms long needles of the X compounds, is detrimental to both the bend and impact resistance and greatly increases corrodibility.

#### THE USES OF ALLOY "N° 12"

For smaller and less responsible parts of the automotive crafts and general castings the alloy N° 12 can be used universally, as it machines well and does not show much shrinkage. The iron of the aluminum ingot used for making the alloy in the presence of excess copper and absence of silicon has a tendency to be located within the primary crystallization pockets so leaving the grain boundaries clean. There it forms peculiar aggregates (a variation of the Chinese scripts) within the individual grains and in this form it influences the corrodibility and the impact strength of the casting much less than in the low-alloyed aluminum. If the price permits, a heat treatment followed by quenching will improve the properties of the casting, particularly by reducing corrodibility, and increasing the impact and bend resistance by 60-80%.

#### • THE GERMAN ALLOY (12-14% Zn and 3% Cu)

A large number of castings where shrinkage is not of much consequence and where the dullness of color is not disadvantageous may be properly made of the "German alloy." This



however is one of the most corrodible of aluminum alloys, second only to those still higher in zinc (for instance the alloy called 2:1). Of its various states the sand cast is the most corrodible. If, however, the molding is done with a liberal use of chills and the casting is subjected to a homogenizing heat treatment (10–16 hours at 450–480°) followed by quenching, the alloy becomes very strong both chemically and mechanically. It constitutes one of the few cast alloys that average 4 ft. lbs. Izod and it has twice the resistance to fracture in slow bending of the alloy N° 12.

#### CHEMICAL MACHINERY AND Al-Si ALLOYS

For castings comprising parts of chemical machinery the non-modified 10.5% silicon alloy (silumin) and the modified 13% silicon alloy (Alpax) are undoubtedly the best possible. They are also quite strong, although not very rigid. In the absence of iron (not above 0.3%) they show an Izod of 2.5 ft. lbs. in the modified and 1.25 in the non-modified state. In the presence of more than 0.3% of iron they are apt to be more or less porous and their impact and bend resistance drop heavily.

#### THE Y ALLOY AND THE NAVY ALLOY

Finally, where non-complicated parts (ribbed rods, shaftings, piston stocks, reinforced plates and tubings) have to be executed by casting, two compositions will be found superior to any other. One is the U. S. Navy alloy (1–1.5% Cu + 1.5–2% Mn), which has the advantage of a very low corrodibility, high impact and bend resistance, reasonable ductility and a very reliable tensile strength with no heat treatment being involved. Chill casting is, however, required to develop its highest properties; a slight anneal may add much to its chemical resistivity.

The second is the Magnalite or the Y alloy (1.5% Mg, 4.0% Cu, 2.0% Ni). This alloy is particularly suited for chill castings. In this state aluminides of nickel and copper form at first a network of a double compound and the alloy exhibits no particularly high properties. On subjecting the

alloy to a heat treatment at 520–530° C., the copper goes into solid solution and the whole mass recrystallizes, with the grain boundaries running between the particles of nickel aluminide, the latter becoming in this way enclosed by the grains of the ground mass; these grains themselves are the smallest among all aluminum casting alloys known. A subsequent heat treatment at 150–175° C. increases the hardness of the castings by raising it to 120 Brinell with no less than 44,000 lbs. strength and a reasonably good ductility.

The resistance to bend in the chill cast Y alloy is high, much higher than in any other casting alloy, and it becomes still higher after the first heat treatment and quenching, the impact resistance changing analogously.

If high impact strength is to be preserved the alloy ought not to be allowed to reach the limits of tensile strength and hardness in the second heat treatment. It is only too easy to have the impact resistance reduced from 5.9 to less than 1.00 ft. lbs.

Magnalite can also be used for sand castings with an identical heat treatment. In this case however only a part of the copper will combine with the nickel to form a double aluminide, and this will stay in a peculiar form of oval aggregates radiating from an elongated central core. Most of the nickel forms a fan-like eutectic heavily reinforcing the grains.

Magnalite is not essentially a sand casting alloy. There are plenty of alloys that will wear better and show the same strength with less care and less cost. Sand cast magnalite in the heat treated state ought to be used only when exceptional impact strength and resistance to bend are desired. If not over-heat treated the castings of magnalite will be 2.5 times stronger in bend than the N° 12 alloy and show 1.7 ft. lbs. Izod.

#### MAGNALITE — AN OVERLOADED ALLOY

It may be seriously asked if the high amount of magnesium used in magnalite castings is actually necessary. There is hardly a good reason for it unless it is expected to remelt

the alloy many times. In this case of course, small amounts (up to 0.2%) of magnesium burn away in each remelt so that the alloy may be remelted four times at least, before it starts to lose the power of hardening.

On the other hand this amount of magnesium overloads the alloy very heavily with additional constituents and particularly with magnesium oxide. To compare:—an alloy containing 5% copper, 1.0% manganese, 0.5% iron and 0.4% magnesium can be rolled with ease and its fractures are lustrous. The Y metal can be forged with difficulty and fractures incurred in forging have a gray earthen appearance. Probably just as high a hardness and strength could be obtained in the chill cast state by reducing both magnesium and nickel by 0.5% each.

#### THERMAL CONDUCTIVITY OF ALUMINUM AND ITS ALLOYS

Aluminum, both pure and alloyed finds a great number of applications in which it is required to transmit a large amount of heat rapidly; it is sufficient to mention only two such cases, namely internal-combustion engines and the aluminum kettles used in the chemical industry. It is natural, therefore, to inquire how efficient this metal and its alloys are as agents for heat transmission. We shall first examine the problem in an analytical way and conclude with certain experimental suggestions.

The mechanism of heat transmission is still a matter of speculation. Does it involve a steady exchange of electrons between adjacent atoms of the metallic aggregate, or is it a result of increased vibratory energy of the atoms themselves, or both? A definite answer cannot yet be given.

Physical science lays much stress upon the apparent analogy between electric and thermal conductivities, resulting in the frequent statement that the conduction of heat follows the same general type of laws as that of electricity.

So far as our knowledge of alloys goes, two facts are already established: first, that the electric conductivity of the main metal is greatly diminished as soon as the added element

enters into solid solution with it: second, that the loss of conductivity per unit of the added element is most pronounced at the very first addition.

While it is true that the thermal conductivity of solid solutions diminishes with additions of the alloying element, following the same type of law as that governing electric conductivity, the analogy stops here and the quantitative relations are quite different. Let us compare, for example, the electric and thermal conductivities of certain copper alloys which have been far more extensively studied. The figures are compiled in the following table:

	Electric Conductivity	Thermal Conductivity
I. Copper-zinc brasses:		
Pure copper	100%	100%
1% zinc	87	98.5
33% zinc	22	40
II. Copper-tin bronzes:		
Pure copper	100	100
1% tin	60	91
9% tin	11	20
III. Copper-aluminum bronzes:		
Pure copper	100	100
1% aluminum	40	93
9% aluminum	14	45

We may therefore say that the diminution in heat conductivity is much less important, even theoretically, than that of electric conductivity.

The second important fact is that the effective heat conductivity of the metallic wall of a given vessel is much more subject to our control than the electric conductivity of a given conductor. The latter depends upon the length of the conductor which we cannot control, and upon its cross-section, which we can control (by increasing it) only to our general disadvantage. Heat conductivity, on the contrary, depends upon the heated surface of the vessel, which we cannot always

control, and upon the thickness of the wall, which we can control to our advantage.

To illustrate: Suppose we desire to make an annealed cable of 33% brass, hoping to take advantage of its cheapness and its 60% higher strength as compared with copper. Assuming that the electric power losses must not be increased, we shall have to increase the cross-section some 4.5 times. As a result, nothing is gained by the higher strength of brass, while the cost of the construction will be tremendously increased, nullifying all expected advantages of the cheaper metal.

Suppose, however, that a certain chemical vessel made of copper has to have a wall  $\frac{1}{2}$  in. thick to withstand certain internal forces. The same vessel if made of a 32% brass will require a wall only  $\frac{5}{16}$  in. thick and its heat conductivity will be above 50% of that of the copper wall.

Hence, the substitution of an alloy with low electric conductivity for the pure metal will always entail either increased power losses in the conductor or an increased weight of conductor together with an increased cost of installation. On the other hand, the substitution of an alloy with low for one with high heat conductivity may not affect at all the effective conductivity while also affording the advantage of a smaller weight (and possibly cost) provided the alloy is stronger and the chemical conditions permit its use.

A third important consideration lies in the fact that the rate of heat flow in a given system or a given apparatus (gas engine, kettle, etc.) depends much more upon the conductivities of the heat-generating and the heat-absorbing media than upon that of the separating wall itself. A well-stirred mobile liquid will absorb more heat per unit of time from a wall of porcelain than a viscous and unstirred material from a wall of silver. In fact, the substitution of a vapor condenser made of good heavy glass for one made of pure copper results in a drop of only 50% in efficiency, all other conditions remaining identical, whereas on the basis of relative conductivities alone, not more than 5% efficiency might be reasonably expected from

the glass condenser. It is particularly important to remember that the thinnest deposit of a crystallized salt or mud formed in a chemical apparatus, or of carbon in a gasoline engine, will almost completely offset the difference in total heat conduction between a high-conductivity metal and a low-conductivity alloy.

Turning now to aluminum we find at once that even its electric conductivity is only moderately affected by alloying within the solid solution ranges. Taking the conductivity of the purest aluminum as 100%, we find the electric conductivity dropping to 70% for a quenched 4% copper alloy; to 70% for a quenched 16% tin alloy; to 63% for an annealed 17% zinc alloy; and to 50% (probably) for a well annealed 10% magnesium alloy. By analogy with the copper alloys, we may therefore expect the heat conductivities of the above-named solid-solution aluminum alloys to be at least as near and probably nearer to that of the pure metal.

Aluminum alloys of the industry, however, are rarely solid solutions. Most of them, particularly in the cast form, represent a mixture of a solid solution (ground mass) with one or many aluminides. While in copper alloys, furthermore, the electric and heat conductivities of alloys having a complex structure are generally affected nearly in direct proportion to the volumes of the constituents, this rule does not appear to hold in complex aluminum alloys. For example, in a 30% nickel alloy the electric conductivity drops to 28% and in an annealed 18% copper alloy to 62%. Even if the whole amount of nickel or copper aluminide (about 50% and 25% respectively by volume) should represent a non-conductor, the specific conductivities of these alloys ought not to drop below 50% to 75% respectively.

Fig. 87 represents the influence of various additional elements upon the conductivity of aluminum. Data laid in its basis were undoubtedly crude and it may not serve but for the very rough approximation in the absence of more exact determinations. (Guerbler Metallographie.)

One must therefore conclude either that our knowledge of

electric conductivity constants for aluminum alloys is at fault, or that there is some still unknown cause which tends to reduce their electric conductivities considerably below what would be

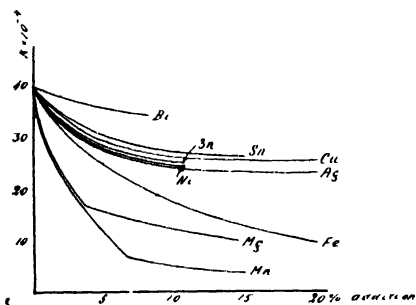


FIG 87.

expected on the principle of additivity; and the same may, of course, be true for thermal conductivities.

A number of aluminum alloys were tested as to heat conductivity by members of the British light alloys subcommittee of the air-navigation com-

mission. Some of the tests were made at two different points of temperature. In most cases the figures obtained for the regularly used alloys fall well within the range of 65 to 80% of the conductivity of the pure aluminum.

In a few cases the mentioned data show thermal conductivities as low as 50% that of pure aluminum, the absolute conductivity of the latter being  $0.51 \frac{\text{calories}}{\text{cm}^2 \cdot \text{sec.} \cdot 1^\circ}$ .

A more complete table of thermal conductivities is presented on page 223.

There are, however, a good many reasons to doubt the correctness of these low data. It can be accepted, in general, that a good industrial aluminum alloy will not show less than 70% of the heat conductivity of the pure metal. It is not impossible, furthermore, that certain commercial alloys with electric conductivities substantially higher than 70%, may possess heat conductivities ranging around 80% in dense, sound castings.

To resume:

1. The heat conductivity of an aluminum alloy is substantially that afforded by the aluminum metal present as such in the alloy.

2. The heat conductivity of an aluminum alloy can neither exceed that of aluminum metal nor can it be so low as to make

TABLE XVI.—HEAT CONDUCTIVITY OF ALUMINUM ALLOYS

Alloy	Composition	State	Cond-ty calories cm <sup>3</sup> sec. 1° C.	Authority
1st grade Al	<0.3% impurities	Rolled, annealed	0.594	Lees
Good aluminum	0.4% Fe, 0.1% Si	"	0.400	Donaldson
2nd grade Al.	0.51% Fe, 0.24% Si	Cast	0.444	Matsumoto
"	"	Wrought, hard	0.478	"
Duralumin	4.3% Cu, 0.5% Mn, 0.4% Mg, 0.9% Fe, 0.4% Si	Cast	0.292	"
"	"	Cold rolled	0.354	"
"	"	Rolled, annealed	0.414	"
"	5.3% Cu, 1.15% Mg, 0.5% Mn, 0.8% Fe, 0.45% Si	Cast	0.283	"
" Y "	"	Cold rolled	0.325	"
"	"	Rolled, annealed	0.382	"
" Y "	4.4% Cu, 0.9% Mg, 2.05% Ni, 0.7% Fe, 0.5% Si	Cast	0.310	"
" 12 "	"	" , annealed	0.351	"
" 12 "	"	" , quenched	0.316	"
" 12 "	"	" , annealed	0.400	"
" 12 "	"	"	0.240	"
" 12 "	With 1% Mn	"	0.335	"
" 12 "	" 1-2% Fe	"	0.380	"
" 12 "	" 3% Ni	"	0.350	"
Piston alloys	12% Cu, 0.6% Fe	"	0.380	Light alloy Report
"	With 3% Ni	"	"	"
"	" 1% Mn	"	"	"
"	" " " "	"	0.340	"
"	" " " "	"	0.260	"
"	" " " "	"	0.313	"
"	" " " "	" , annealed	0.433	"
"	" " " "	"	0.386	"
Alpax	14% Si	"	0.310	Matsumoto
German alloy	12-14% Zn + 3% Cu	"	0.320	"
"	" " " "	" , annealed	0.233	"
" E " alloy	20% Zn, 2.6% Cu, 0.55% Fe, 0.35% Si	" , annealed	0.258	"



the use of a given alloy questionable from the viewpoint of efficient heat transmission provided the article itself is sound.

3. The specific media, the conditions under which an aluminum article operates, and the variability of these media and conditions all tend to nullify the differences in heat conductivity and therefore to render the problem of good conductivity a matter of slight importance.

Nevertheless it frequently happens that a person in the aluminum industry is confronted by the claim of an inventor or competitor that his alloy has a much higher heat conductivity. In such cases a theoretical analysis of the situation usually leads nowhere and the only substantial argument rests on an actual determination of the heat conductivity of the new alloy.

The experimental difficulties of this operation may seem large but they are not actually so. A fine potentiometer sensitive enough to measure voltages of 0.01 milli-volts costs only \$200, and with this at hand a little skill will enable one to obtain heat conductivity figures correct to 5% or better. The method of testing is as follows:

Figure 88 shows an apparatus which has been successfully used for this purpose. This consists of a source of heat H, a vessel containing boiling water which is thus automatically kept at a constant temperature, and a heat receptacle or calorimeter C which measures the heat conducted from the source H through the test bar D. The test bars may be  $\frac{1}{2}$  in. square and 6 in. long. These are soldered into square holes in the sides of H and C with about 1 in. at each end protruding into the vessels. Two copper-constantan thermocouples made from No. 40 wire (thin enough to minimize heat conduction) are fastened into small holes drilled into the sides of the bar at a distance of 2 in. apart. These couples measure the temperature drop along the middle 2 in. of the bar, within which distance the heat flows in practically parallel lines. The entire apparatus, except the bottom of H, must be carefully covered with insulation to minimize errors due to losses, and a screen S must be placed between the burner B and the

calorimeter C. The temperature of the water in the calorimeter is read by a thermometer graduated to  $0.1^{\circ}\text{C}$ . and this temperature is kept uniform throughout the mass of the water by a small stirrer with a glass shaft driven by an electric motor.

After setting up the apparatus as shown, the water in H is heated to boiling and conditions are allowed to become constant while maintaining the temperature of the water in C about  $5^{\circ}\text{C}$ . below the room temperature by the addition of

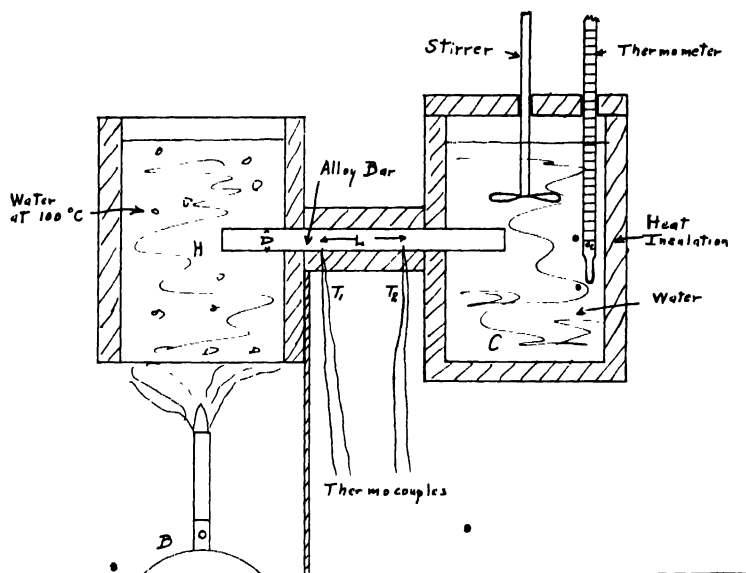


FIG. 88.

small pieces of ice from time to time. When the temperature readings become stable for several minutes the ice is removed and the time required for the temperature of the water in the calorimeter to rise from  $5^{\circ}$  below to  $5^{\circ}$  above room temperature is noted. Careful readings of the voltages of the thermocouples are made during this time; these require an accurate potentiometer as they are a most important factor in the calculation of conductivity. When the run has been completed the

weight of the water in the calorimeter C is determined and the conductivity is calculated by the following formula:<sup>1</sup>

$$\text{Conductivity (calories per sq. cm. length per } ^\circ \text{C, per second)} \dots\dots\dots = \frac{W (T_4 - T_3) \times L}{t \times D^2 \times (T_1 - T_2)}$$

W = weight of water in calorimeter in grams, plus water equivalent of calorimeter obtained by multiplying weight of calorimeter by the specific heat of the metal of which it is made.

T<sub>4</sub> = temperature of water at end of the test, in  $^\circ \text{C}$ .

T<sub>3</sub> = temperature of water at beginning of the test, in  $^\circ \text{C}$ .

L = length of bar between thermocouples, in centimeters.

t = time of test, in seconds.

D = width of the square test bar, in centimeters.

T<sub>1</sub> = temperature of the first thermocouple, in  $^\circ \text{C}$ .

T<sub>2</sub> = temperature of the second thermocouple, in  $^\circ \text{C}$ .

An example of a test made according to this method is given below:

$$\begin{array}{r} W = 1175 \text{ grams water} \\ \quad 50 \text{ grams water equivalent of calorimeter} \\ \hline 1225 \end{array}$$

$$T_4 = 29.7^\circ \text{C} \quad T_3 = 22.7^\circ \text{C} \quad L = 5.08 \text{ cm.} \quad D = 1.27 \text{ cm.}$$

$$T_1 = 60.5^\circ \text{C} \quad T_2 = 35.5^\circ \text{C} \quad t = 54 \text{ minutes or } 3250 \text{ seconds}$$

The absolute conductivity is thus

$$\frac{1225 \times (29.7 - 22.7) \times 5.08}{3240 \times 1.27^2 \times (60.5 - 35.5)} = 0.33$$

A much more refined method and apparatus is described by Donaldson in J. Inst. Metals, 1925.

<sup>1</sup> The description of the apparatus and method of testing was obtained by courtesy Mr. G. D. Bagley, of the Union Carbide and Carbon Research Laboratories.

PART VI  
STRUCTUROGRAPHY<sup>1</sup> OF ALUMINUM AND  
ITS ALLOYS

<sup>1</sup> A constructive word used because of its appropriateness to the matter described in this chapter. ●



## INTRODUCTION

THE value of structural investigations of a metal for its technology is too obvious to require explanation. On the other hand, the real connection between the structure of a metal and the control of the properties of a product is too intangible to be coached in any descriptive terms.

Starting from metallic aluminum one has to analyze in the first place the structural conditions prevailing in the notched bars—practically the only shape in which aluminum is brought on the market from the aluminum reduction plant. If the metal is substantially free from contamination (99.8% pure) the ingot crystallizes in the following manner: the bottom and the sides of each section are built up for a short distance of a layer of small crystals due to the high rate of cooling and solidification in contact with the mold. Beyond this layer the ingot consists of a large body of elongated columnar crystals, reaching almost to the top of the ingot. A beautiful picture of a cross section of a pure aluminum ingot is shown by F. Flick (*Etching Aluminum and Its Alloys*. Tr. Am. Inst. Min. & Met. Engrs., 1925, Vol. 71, page 816). When the virgin ingot is remelted and cast into billets for rolling or extrusion the type of crystallization becomes more complex. The layer of fine crystals at the circumference of the billet and the columnar crystals directed toward its center or central line persist. However, the columnar crystallization stops at some distance from the center and comparatively small equiaxial crystals form the core of the billet.

Each foreign substance present in aluminum affects the type of its crystallization. The resulting changes depend on the individual character and the amount of the addition.

Those entering into solid solution in aluminum tend in a general way to produce uniform equiaxial grains. The size of the latter decreases with the increase in the amount of addition.

In this very same case, when a solid solution forms, chemical differences within each crystalline grain are liable to take place. Usually the core of each grain will be leaner and the circumference richer in the added element or in the contamination.

When the addition or contamination forms a separate phase, crystallizing in advance of the crystallization of the ground mass the general aspect of a cross section of the ingot or billet will be entirely different. The size of the grains may become so small as to be almost unidentifiable provided the second constituent is present in small quantities only. With a further increase in its amount it crystallizes in chains of dendrites taking their start at the surface of the billet, the bulk of the metal crystallizing between them. The resulting structures look like the columnar crystal bodies of pure aluminum but are of an entirely different nature, each column being built up of needles.

When the second component forms a phase that crystallizes secondarily, *i.e.*, in the form of eutectical mixture with the aluminum, its influence is seen in the decrease of the area occupied by the columnar crystals and the increase in the area occupied by the small equiaxial crystals of the core. The core crystals vary in size according to the conditions of cooling, the fluctuations never being large. The reason why a constituent crystallizing eutectically compels the main metal to form a greatly increased number of crystallization nuclei and helps in distributing them more evenly is not yet entirely clear.

#### STRUCTURAL INFLUENCE OF WORKING AND ANNEALING

When the billet is subjected to rolling, drawing or extrusion, its metal flows, *i.e.*, each crystal breaks up along its cleavage planes in individual lamellae sliding along each other.

In this manner the initial crystal may finally form either a fine fibre or a fine leaflet according to the type of the mechanical operation.

The annealing process relieves the strains existing between the lamellae or fibres of the worked metal and makes them independent each from another to the extent of the formation of new grains, *i.e.*, recrystallization. The material of which the old boundaries were formed (intergranular cement) may be either so far disintegrated as to make it impossible to trace the old boundaries or it may remain in the same relative position.

The annealing process leads also to a chemical homogenization of the alloy, each grain becoming a more or less uniform crystal with little or no variations in the chemical composition within its boundaries. The disintegration of the old grain boundaries due to working and the chemical homogenization of the grains due to annealing may take place to a variable extent.

All the features above mentioned are of substantial importance to the technology of aluminum and its alloys and must therefore be studied in detail in each particular case. This study may be macro and micro structural according to the way the examination is made. One uses either low magnification (1–20 times) in the macrostructural, or high magnification (50–1000 times) in microstructural work on aluminum.

The study of macrostructures (otherwise called textures) is still in its very infancy. The results of studies so far accomplished represent usually more or less beautiful pictures of the crystalline state in metals and hardly more. There is no doubt however but that an accumulation of material in this field will finally result in a clear understanding of the process of crystallization and will enable the foundryman to control it more accurately.

Microstructural studies lead to much more definite results at the present time. They usually yield knowledge of the grain size, chemical heterogeneity of the crystals, mechanical



strains and the additional constituents natural or artificial in either a primary or an eutectic crystallization.

#### PECULIAR FEATURES OF THE EUTECTICS IN ALUMINUM ALLOYS

It should be stated at this point, that the so-called eutectic structure, meaning a very intimate mixture of two different constituents in a definite proportion, practically does not occur in aluminum alloys. A definite alloy of lead with either antimony or tin, or copper with silver will show in the cast state the primary grains of the main metal surrounded by a strictly constant volume of a heterogeneous mass, the particles of which have no definite shape and only a very small size. The power of crystallization of both the main metal and of the secondary constituent in aluminum alloys is usually so strong and the physical attraction between these latter so small, that grainlets of the secondary constituent stand out sharply and give no indication of belonging to an eutectic. Even in that most definite case of an eutectic as it occurs in aluminum silicon alloys, one finds large fields of aluminum and large grains of silicon. Both appear as being crystallized without influencing each other. It takes a certain specific process to make it impossible for the silicon grains to form large crystals and only in alloys thus refined is a true eutectic observed.

#### THE TECHNIQUE OF STRUCTUROGRAPHIC INVESTIGATIONS

In the same manner as with other metals the samples of aluminum or its alloys must undergo a process of preparation before they can be examined for their structure. This preparation consists in first taking the sample, then grinding and polishing its surface so as to remove all scratches.

The difficulties of the total work vary with the hardness of aluminum alloys over a rather wide range. From a hardness of 16 Brinell which is that of the purest aluminum ingot one may go in a continuous way until a hardness of 165 Brinell is reached for hard rolled duralumin. In the face of

this fact it becomes impractical to give instructions to be applied painstakingly on every occasion.

The most difficult case is that of pure aluminum and of a few alloys used in the wrought shape without any artificial hardening. In this group belong, among the technical alloys, pure aluminum, aluminum copper alloys up to 3% Cu, aluminum magnesium alloys up to 3% Mg and aluminum manganese up to 2% manganese, besides those of the Al-Fe, Al-Ni, etc., systems which have only a theoretical interest. Alloys containing substantial amounts of zinc or large amounts of copper form another group much more easily prepared for microscopic work, while the alloys amenable to heat treatment can be prepared most easily.

With aluminum alloys of the soft group the following conditions must be observed in their preparation for the investigation. First of all the sample may not be separated by the use of a cutting-off wheel. It drags the metal and distorts its grains to a great depth. Consequently it takes a very long grinding and polishing to remove all traces of distortion. Cutting by hand with a hack-saw or mechanically with a band-saw helps to obtain a good surface, and a lubricant (kerosene) must be used liberally. With hard alloys not much care is necessary in the separation from the sample; any method leads practically to the same results.

#### Grinding •

The operation of grinding has been the subject of much experimentation by a number of workers. It is a fact that grinding in the regular way as used in the laboratories of iron and copper mills is likely to lead to deep deformations in the metal due to the dragging action of the abrasive upon the surface of the sample. Besides, the metal removed by grinding easily enters into the tiny scratches upon the surface of the sample and the whole of the latter becomes covered with a thick film of distorted metal. Once this happens, no polishing will remove the distorted metal and the etching results in a network of dirt instead of the real structure. There is no exag-

geration in stating, that practically all photomicrographs of aluminum alloys published before 1922 represented mainly the structure of the dirt on their surfaces. Only since 1922 did the nature of this distorted film begin to be understood and a number of workers obtained good results in the microstructural examination of aluminum alloys by its careful elimination.

It is important to state in connection with the nature of this dirt that some workers believed it to be due to the particles of the abrasive sticking to the surface of the metal. The author's experience has convinced him, however, that no such thing occurs, *i.e.*, the abrasive does not become imbedded in the metal.

The best way of avoiding the formation of the distorted layer consists in the liberal application of some oily substance soaking the surface of the grinding paper. Plain kerosene is at least as good as anything else so far proposed and only for the sake of completeness must it be stated that a number of workers soak the emery paper discs either in a solution of paraffin in kerosene, or in molten paraffin. Both methods lead to an unnecessary complication only.

Many authors recommend that the grinding as finished on paper N° 0000 be continued on cloth using in succession two strong abrasives, namely alundum and tripoli, before the actual polishing is resorted to. It was the experience of the author however that neither alundum nor tripoli form a good grinding media for aluminum. They hardly can be used with oil, and when used with water they cover the surface of the sample with a film of metallic and abrasive grit and this film is difficult to remove.

The softness of the plain and low alloyed aluminum causes it to flow abundantly during the process of grinding. Scratches upon the surface are quickly covered and hidden by the floated metal if the grinding is done in one direction. A frequent turning of the sample by  $180^\circ$  during grinding helps to minimize these difficulties.

A number of authors recommend magnesia applied to fine

cloth for polishing the aluminum, and undoubtedly this polish actually leads to good results. It is not very convenient, however, inasmuch as the magnesia-covered cloth alters quickly in the air due to the formation of magnesium carbonate and becomes gritty.

There is no need to look for any other polishing medium but the regularly and universally used alumina. This latter is so uniform, so unalterable and so universal in its action, that it is perfectly reasonable to apply it in each case. It is quite possible for instance to remove all scratches by beginning to polish on a disc of cloth covered with a substantial amount of alumina thoroughly moistened, and finishing with very little alumina and an almost dry cloth. After polishing on alumina the sample is subjected to a final polish on a piece of silk-velvet covered with soap. In this way all scratches and dirt can be removed quickly and easily. To resume:—grinding upon oiled emery papers N<sup>os</sup> 1, 0, 2-0 and 3-0, rough polishing on alumina and a good woolen cloth and finishing with soap on fine velvet permits the preparation of any sample of a soft aluminum alloy faultlessly in about 20 minutes.

#### Hand versus Machine Grinding

Many authors suggest grinding by hand for the preparation of aluminum samples. This is positively a wrong solution. Turning back from machinery to hand work is entirely impossible in the days of quantity production and high wages. Examination of structures also has to be run on a quantity production basis and the pertinent technique must be as inexpensive as possible.

On the other hand the use of regular small discs of 6" in diameter rotating at a speed of at least 600 R.P.M. as generally found in the laboratories of the steel mills may not be considered a most desirable method. No doubt they can be used and were used by many workers with good success, but a definite improvement must be introduced in the process to speed up the work. The use of large discs of about 10 to 12" in diameter running at a low speed of 200-400 R.P.M. ex-

pedites the work and makes the results more comparable with those of the tedious preparation by hand (elimination of circular scratches).

#### EXAMINATION IN THE UNETCHED STATE

The technique of etching aluminum alloys was very imperfect until recently. No reagent was known which would afford the investigators a means of showing the various aspects of the structure of an alloy. To show the grain size, chemical heterogeneity within the grain, and at the same time to identify the secondary constituents of an alloy was next to impossible. Consequently a number of authors preferred to study aluminum and its alloys in the unetched state. Each constituent of an aluminum alloy is much harder than the aluminum matrix and possesses much more selective power to absorb light. Therefore, particles of these constituents can be seen without etching.

Examination in the unetched state is very important and is practically the only method by which the tiniest defects in aluminum alloys may be detected. Small pin-holes and film inclusions are clearly visible on a well polished unetched surface. In the etched state they are frequently masked by light reflexes and by secondary chemical action. In this connection the technical paper N° 241 of the U. S. Bureau of Mines (Blowholes, Porosity and Unsoundness in Aluminum Alloy Castings), by R. Anderson, must be recommended for study before examining aluminum ingots or castings for defects.

In all cases however, when it is required to establish the nature of crystallization either in the cast or in the wrought state, or the flow lines in a worked metal or to reveal the detail of more intimate microstructure, etching the alloy becomes unavoidably important. In the study of macrostructure, etching outlines the "primary pockets" and the grains. The task is simple and a rather large number of reagents act quite efficiently. A surface which is to be investigated for its macrostructure may be etched by solutions of sodium hydroxide, nitric, hydrochloric, and, best of all, hydrofluoric

acid.' The concentrations may differ largely and for each reagent one can find a concentration, temperature and duration of etching which develops good macrostructures.

On this occasion emphasis must be laid upon the fact, that the macrostructure of aluminum alloys is a much more difficult subject of study than that of iron and copper alloys. A piece of an iron or copper alloy may be ground on a comparatively rough emery paper or cloths N<sup>os</sup> 1 and 0 only, and yet a deep etch with a suitable reagent will reveal beautifully the macrostructure with all scratches from grinding completely gone. With aluminum it is different. The etching action seems to take place preferentially at the scratches and the macrostructure becomes blurred by the unevenness of surface. In a few instances this blurring does not go too far; in the largest majority of cases however no good macrostructural study can be made unless the piece is just as well ground and polished as if intended for a microscopical examination with a high power lens.

#### ETCHING FOR MICROSTRUCTURAL STUDY

For the examination of the microstructure there are two most important requirements an etching medium is called to fulfill. It has to reveal the secondary constituents in the most definite manner, *i.e.* permitting their identification and differentiation if a number are present. It must also reveal the chemical inhomogeneity of the grains by the variation of the depth of etching, thus producing "cores" or "dendrites" in the non-uniform grains.

In certain cases there is still another task to fulfill, namely to obtain a clear and definite development of grain boundaries, permitting the measurement of their size. These three goals reached and the sample showing no pitting, the etching reagent may be considered suitable.

Two reagents were used in a general way in the past for revealing the structures of aluminum alloys. One—a solution of sodium hydroxide, the second—of hydrofluoric acid. Neither of them is, however, universal. A number of alloys will not show any grain boundaries when etched with hydro-

fluoric acid due to the excessive pitting. Neither of the two reveals the chemical heterogeneity in alloys representing solid solutions of copper in aluminum, though both will show it definitely but none too smooth in alloys of aluminum with zinc.

A plain etching with either one of these reagents usually leaves the surface of the sample in a somewhat dirty state. This is due mainly to the precipitation of iron, copper or zinc during the process of solution, and can be removed by the action of moderately concentrated nitric or chromic acid. The sample must be immersed in either one immediately after the etching, otherwise the deposit sticks to the surface.

Both sodium hydroxide and hydrofluoric acid are apt to produce a substantial pitting around each particle of a secondary constituent, if allowed to act for an extended time. However, they undoubtedly reveal the grain boundaries in most cases and while the developed structure is usually somewhat blurred it can be relied upon for the estimation of the grain size. Secondary constituents are usually blackened when etched with these reagents and can not be differentiated or identified on the basis of individual colors or shades. In a great many cases the pitting around these constituents robs them of their original sharp outline and on this account even their shape escapes identification.

Practically every mineral acid can be applied to the etching of aluminum, and nitric acid in spite of its generally slow corrosive action on aluminum does not form any exception. In fact a number of authorities consider it in concentrations of 20 to 25% to be the best reagent for the identification of different secondary constituents as for instance copper, iron, nickel and manganese aluminides. It is used comparatively hot (at 70° C.) and the sample is immersed for 5-30 seconds, further action being stopped by dipping in cold water. This method of etching initially developed by Hanson and somewhat modified by Dix is called the *nitric acid quench*.

The author found that even cold solutions of nitric acid are suitable for the identification of compounds in cast alloys

and also well adapted for the development of grain boundaries and cored structures inside the grains, provided the action lasts for many hours. Specimens immersed in nitric acid of 20 to 25% for a period of 1 to 6 hours will be etched fairly well. They will show besides a number of dark wavy lines indicating the spots of selective corrosive action.

In certain cases etching a sample consecutively by hydrofluoric and hydrochloric acids as suggested by Czochralski helps to develop grain boundaries with good success. A variation on this method consists in etching with a mixture of hydrofluoric and hydrochloric acids as suggested by R. Flick. This kind of etch is particularly good for macrostructural investigations of various alloys. In a number of cases, however, especially with alloys containing larger amounts of magnesium, the grain boundaries cannot be developed at all by an acid etch, while an etch with sodium hydroxide leaves behind a heavy tarnish. In this case, etching by a boiling solution of sodium hydroxide (5-10%) followed by cold hydrofluoric acid and finished by immersion in cold 30% nitric acid helps to produce the desired results. Frequently this treatment has to be repeated once or twice.

By far the best, although by no means universal, method of etching aluminum alloys is the one developed in the laboratories of the Union Carbide and Carbon Corporation by J. R. Vilella. The reagent used consists of a solution of hydrofluoric and nitric acids in glycerine. This solvent slows down the action of the hydrofluoric acid making the attack more uniform and the surface free from pitting while nitric acid helps to automatically maintain it in a clean state. The usual concentration calls for three parts glycerine, two of hydrofluoric acid and one of nitric acid by volume, though variations in every direction are permissible and may be found advantageous in specific cases,

It happens, sometimes, that a sample is ready for microscopical investigation right after the final polishing and the first etch. In the majority of cases, however, a discontinuous layer of distorted metal will be found to remain upon the



surface which frequently leads to entirely erratic conclusions. Therefore it is advantageous to retouch the specimens in each case on fine velvet with soap and a little alumina and to etch them again. If the structure shows no more changes this ends the question. If it changes and changes for the better, *i.e.* becomes clearer and more definite the same treatment may be advantageously repeated once more.

### DESCRIPTION OF INDIVIDUAL CASES

#### COMMERCIAL ALUMINUM METAL (Plates 1-13)

A billet of the purest commercial aluminum (99.7%) when polished and etched with a mixture of hydrochloric and hydrofluoric acids (Flick's method) will show a macrostructure like that of Fig. 1. The columnar crystals occupy almost the whole section and a few smaller equiaxial grains crystallize at the center of the billet. The size and shape of the central part of the billet depends on two main features, namely the amount of iron present and the temperature of the casting. With a reasonably small amount of iron (not above .4%) and a low temperature of casting we obtain an increased core with large grains (Fig. 2). A high temperature of casting will produce smaller grains and a larger core. A good instance of this latter case is shown by E. Seidl and E. Schiebold (*Z. F. Metallkunde*, 1925, p. 221). There the iron totalling .3% has been continuously rejected from the circumference of the billet to its center during solidification and became so enriched at this point as to strongly affect the size of the grain. With a further increase in the amount of iron the size of the core becomes still larger and the size of the individual grains of the core decreases. Finally with .7% Fe in small and .9% in large billets no individual grains will be discerned even at a good macromagnification. The etching pits forming around iron aluminum particles become too close and the etching action around them too quick to permit the grain boundaries to be developed.

Fig. 3 shows the microstructure corresponding to Fig. 2. It relates to the central part of the billet and shows the equi-

directional distribution of the chainlets of iron aluminide. Fig. 4 represents the microstructure at a corner of the same billet. The amount of iron aluminide is here much lower. The  $\text{FeAl}_3$  in Fig. 4 crystallized in the same direction as the columnar crystal growth, while its distribution in Fig. 3 shows that it probably was instrumental in producing the equiaxial grains of the core.

Figs. 5 and 6 represent the macrostructures of the 99.7% aluminum as cast in a chill and a sand mold respectively. In the first case the columnar crystals reach practically to the center of the chill cast bar. In the second, with the velocity of cooling much slower, the crystal growth is less regular.

Neither in these two cases nor in those presented by Figs. 1 and 2 may the visibly individual grains be actually considered as representing continuous crystals. In fact their outlines are built up from those particles of impurities (either aluminum oxide or iron aluminide or both) which were rejected from the initial nucleus of the grains. Along these boundaries we undoubtedly have the relatively largest amount of these impurities. However, only a part of the total amount of the latter happens to become located at the boundaries. A substantial part stays inside and in the final solidification forms either individual particles or chainlets. When these chains are continuous enough the visible grain as shown in Fig. 5 is actually subdivided in a number of much smaller grains. Accordingly these large visible grains might be properly termed *primary crystallization pockets*. The fine lines which subdivide a pocket into smaller grains are faintly outlined in Figs. 5 and 6 and still better in the beautiful macrographs shown in the mentioned paper by Seidl and Schiebold (pp. 222, 223 and 224).

Figs. 7 and 8 represent the actual structure of large individual pockets. Fig. 7 pertaining to the chill cast condition shows only parallel rows of discontinued iron aluminide particles within the pockets, their main boundaries forming continuous lines. Fig. 8 relating to the sand cast state and presented at a higher magnification shows the real individual crystals

with continuous boundaries as they are formed within a primary pocket.

Figs. 9 and 10 show the macrostructure of the small sized notched bar of second grade aluminum containing about .9% iron. No primary crystallization pockets are visible in this case. These pictures taken with a direct illumination show the ingot to be textureless. However, if examined under an oblique illumination the same cross-sections will show more or less smooth brilliant white fields with grayish crescent-shaped patches.

Figs. 11, 12, and 13 show the microstructure of the bottom, center and top of the above described notched bar. In the bottom part the particles of aluminide are small and uniformly distributed. This is similar to the structure of the core of the billet, with 99.6% Al (Fig. 2). The grainlets of aluminide become larger and more definite in shape toward the top. That is why Fig. 13 shows in spots a similarity to an actual eutectic structure. In this case, however, the outlines of the iron aluminide grainlets are enlarged due to pitting action.

The same ingot when remelted and cast in sand has a much more definitely granular structure as is shown in Figs. 14 and 15. Attention is drawn on this occasion to the cored aspect of each individual grain of the sample. The outside of the grain is light and the core dark. At high magnification this coring is resolved into well defined particles of a precipitate.

When an ingot or billet of commercial aluminum is reheated previous to rolling, the contaminations, particularly those of iron aluminide, change in two different directions. A part coagulates and forms isolated inclusions in the grain. Another part, the larger one, coalesces in such a way that discontinuous chainlets become continuous lines and the boundaries of the secondary grains within the primary pocket gain in sharpness.

Plates 8-11 represent the structures of commercial aluminum sheet of the second grade, *i.e.*, containing at least .6% iron. Fig. 16 pertains to the hard-rolled state and Figs. 17 and

18 to the metal annealed at  $450^{\circ}$  C. for different periods of time. The etching was done by the Flick method, and, while the grains are undoubtedly developed, their boundaries are not continuous and measuring the grain size is comparatively difficult. One has to note the large pits which form around the coagulated iron aluminide (Fig. 18). Figs. 19 and 20 show the same structures at a higher magnification.

Figs. 21 and 22 were obtained by etching with Vilella's reagent and show the boundaries in a much better manner. The grain size can be easily ascertained and one closely perceives the difference between the grain size obtainable at  $300^{\circ}$  and at  $560^{\circ}$ .

Figs. 23 and 24 represent aluminum in the forged state. In Fig. 23 the anneal was only slight and dark lines of excessive corrosion due to weaknesses caused by cold rolling are quite noticeable. Fig. 24 shows the metal much better annealed, all traces of cold work having entirely disappeared.

Fig. 25 shows at 10 d. the surface structure of an aluminum sheet, etched by the method of Flick. In this case the grain size is too large, probably due to excessive annealing.

#### A Combination Etch with Sodium Hydroxide and Hydrofluoric Acid

Still better results can be obtained in the development of aluminum grains by etching with boiling 10% sodium hydroxide followed by immersion in hydrofluoric acid and cleaning with chromic acid. By this method very good pictures of the flow lines due to working can be obtained.

When measuring the grain size of aluminum metal high magnification should not be used. About 15-20 d. is the optimum which leads to very sharp definitions. A large amount of macroscopical investigations of the grain size of aluminum metal was accomplished recently by Feitknecht (J. I. M. 1926). His samples were finished on emery paper N° 000 without subsequent polishing and etched with dilute sodium hydroxide. In spite of this rather simple procedure the results obtained were excellent. The paper mentioned will be

of great assistance to anyone who wishes to study the structure of rolled aluminum in its connection with problems of cold work and recrystallization.

#### ALUMINUM ALLOYS WITH IRON (Plates 14-18)

The importance of the contamination by iron in the study of structure was emphasized in the foregoing pages, and an intimate knowledge of the effects of iron upon the structure of the metal when present in larger amounts is also very valuable. Figs. 26, 27, 28 and 29 show the structures of chill and sand cast bars containing nearly 1% iron. The structure in Fig. 26 is rather analogous to that of the core parts (Fig. 3, Plate 2) of the billet with 0.4% Fe (Fig. 2, Plate 1). Fig. 27 shows the same at 500 d. and one can notice the peculiar structure of the aluminum-iron aluminide eutectic. Fig. 28 shows the same alloy in the sand cast state. The individual particles of the aluminides are large and have a wool-like appearance. In both cases the main part of the micrograph is occupied by the ground mass of aluminum, while, what might seem to be the eutectic hardly occupies more than 10% of it. Accordingly a completely eutectic structure might have been expected at nearly 10% iron. This does not correspond to facts and the peculiar structure is due only to the structural deviations of the aluminum alloys from the general rules of metallography.

Figs. 30, 31 and 32 represent the structure of an alloy with 2.3% iron. Even here, particularly at a magnification of 500 d., the alloy does not appear strictly eutectical. The aluminide of iron is shapeless and is present as long hairy chainlets in the sand cast and as wool-like flocks in the chill cast condition. Annealing the same chill cast alloy at 540° compels the coalescence of the iron aluminide, which takes the shape of equiaxial grainlets covered usually with a dark film of a bluish shade (if examined at 250 d. using an 8 mm. achromate lens).

The very fact that iron aluminide may coalesce and change

from a structure like that of Fig. 30 to that of Fig. 33 is very interesting by itself. In fact it takes a large amount of traveling for the smaller elongated particles to condense so as to form the bigger grainlets. The accepted theory is that a migration within a metal is possible in two ways; either via the grain boundaries or by a dissolution in the solid grain and consequent precipitation. Certain facts, for instance the cored structure of the grains of sand cast commercial aluminum (Fig. 14), lead to the suggestion that a sensible amount of solid solubility of iron in aluminum exists at temperatures not much below the melting point. On the other hand the fact, that the merest traces of iron can be detected microscopically in aluminum metal indicates that its tendency to precipitate at lower temperatures is so high that this solid solution cannot be preserved by quenching.

Fig. 34 shows an exceptionally large crystal of iron aluminide found in the sand cast sample of a 2.3% iron alloy. It is quite remarkable that such primary crystals of iron aluminide may form while the alloy in general does not yet reach the concentration of a definite eutectic. This is another proof for the statement that the crystallization in aluminum alloys is rather complicated and its mechanism requires considerable study.

The black mass near the sharp end of the crystal corresponds to an inclusion of oxide. It is not improbable that there is a definite relationship between the formation of the scattered crystals of iron aluminide and the films of oxide. Here is a specific instance of a "hard spot" in an aluminum alloy.

Fig. 35 shows a chill cast alloy, containing 4.4% iron. Practically all iron aluminide is here in the form of primary crystals. It must be emphasized once more, that the crystallization of the primary iron aluminide develops with such a force, that no residual iron aluminide is left to form an eutectic with the excess aluminum. The structure observed might be described as a promiscuous distribution of needle-like and

rhombic crystals of iron aluminide in a ground mass of crystals of aluminum. Practically no "eutectic" is seen, though it ought to form the only structural form surrounding the primary crystals of iron aluminide.

#### ALUMINUM ALLOYS CONTAINING IRON AND SILICON

(Plates 19-21)

Silicon is the second important contamination in commercial aluminum. No matter how complete the process of refining of the Bauxite ore, small amounts of silica always remain and either electrolytically or by a secondary reduction become precipitated from the melt as silicon metal which dissolves in aluminum. In the absence of iron this silicon, if present up to .4%, will stay in solid solution in aluminum even in the cast state. With a suitable anneal about 1.3% silicon can be absorbed by the solid grains of aluminum.

With iron and silicon simultaneously present the conditions change. It is known that iron aluminide has a much stronger tendency to form in the presence of an excess of aluminum than iron silicide provided only a little silicon is present. Therefore and in accordance with the requirements of the phase rule there is no chance for the aluminide and silicide of iron being present at the same time. It is not excluded, however, that the iron aluminide may contain some silicon or that the silicon present will induce deep changes in the shape of the iron aluminide.

Figs. 37, 38 and 39 show an alloy containing 1.5% iron and 2.0% silicon. Fig. 37 relates to the chill cast and Fig. 39 to the sand cast state. There is no doubt that in the chill cast state the structure does not differ much from that found in the chill cast alloy containing 2.3% iron but practically no silicon. Only the individual small grainlets of iron aluminide become more accentuated and less apt to be surrounded by pits due to etching. Examined at a higher magnification, the alloy shows practically the same appearance of irregular wooly aggregates as in binary aluminum iron alloys. In the sand cast state the conditions are different. The shape of the secondary constituent becomes more definite and shows a

tendency to form either peculiar figures usually called "Chinese Script" or long needles. The latter are supposed to contain silicon and are called the "X" constituent. The relationship of the "X" constituent to the Chinese Script is unknown. It is established, however, that with higher amounts of silicon the "X" constituent predominates, while small amounts of it lead to the formation of the Chinese Script.

These two forms of the iron-bearing constituent differ substantially in their attitude toward etching reagents. The "X" constituent remains practically colorless or slightly gray-pink if etched by Vilella's method, while the Chinese Scripts acquire a dark violet color, which is probably due to the formation of some kind of film. Its coloration can be discerned best under a magnification of 250 d. using an 8 mm. achromate lens.

Figs. 40 and 41 show the structure of the sand cast alloy containing iron and silicon at 500 d. Fig. 40 abounds with the grayish needles of the X, usually shooting out from the eutectical fields occupied by the silicon in excess of solid solubility. Fig. 41 shows a quite different spot where practically no silicon eutectic is present and the iron aluminide or a constituent related to it forms the Chinese Scripts.

Figs. 42 and 43 show the structure of the same alloy but heat treated for 12 hours at 530° and quenched. In both cases the amount of the secondary constituent is much smaller and all of it coagulates either into irregular larger particles of a bluish gray shade or into colorless small rod-like crystals. In the chill cast alloy both types of structure can be found. The larger grainlets represent probably the coagulated silicon, while the little rods are due to the secondarily formed X constituent. In the sand cast alloy no such difference between the two constituents exists. It seems that both silicon and Fe Al<sub>3</sub> coalesce together to form a lone constituent bent on forming straight linear large crystals of a dark violet hue (on etching).

This coalescence of iron aluminide or of an Al-Fe-Si complex takes place spontaneously during the process of solidifi-



cation in alloys containing larger amounts of copper or zinc. The characteristic forms of iron in these cases are illustrated in Figs. 41, 86, 121, 122, 126, 204.

#### ALUMINUM ALLOYS WITH MANGANESE (Plates 22-24)

The structural influence of manganese is analogous to that of iron. Figs. 44 and 45 show the structure of a chill cast bar containing 1.65% Mn and .45% Fe. At the lower magnification there is practically no difference between the structure of this alloy and that of the core of the billet with .4% iron only. At a magnification of 500 d. manganese aluminide appears distributed along the grain boundaries, never penetrating inside and having a tendency to form fine eutectical patches of a simpler shape than observed in the case of iron. Quite probably aluminide of manganese absorbs the aluminide of iron and the structure becomes binary instead of being ternary.

The structure of a sand cast alloy containing 1.95% manganese and 0.2% iron only is shown in Fig. 46. The shape in which the aluminide of manganese crystallizes in this case is rather peculiar. With the iron aluminide tending to form the "Chinese Scripts" the name of "cuneiform" might be even more proper in this case. At any rate the structure is neither eutectic nor does the manganese aluminide form a part of an eutectic network. It simply and completely crystallizes as individualized crystals in the ground mass of aluminum.

Fig. 47 shows the structure of a sand cast alloy containing 5% manganese. A peculiar feature of the alloy so high in manganese is the practical absence of any coloring upon the large crystals of manganese aluminide, while the cuneiform crystals described above are always colored a pale pink.

Recently the structures of alloys of aluminum with manganese were studied in detail by Daniels (J. Ind. Eng. Ch., 1926; v. 18, p. 125) and also by J. Vilella. Each found that under certain conditions, particularly in the presence of iron (Vilella), the manganese aluminide has a tendency to form rows of similarly shaped though irregular crystals. These rows remind one of the disconnected vertebrae of a prehis-

foric animal and were given the name of "spines" by Daniels.

When aluminum manganese alloys are hot forged or rolled the manganese-aluminide present is broken up and scattered through the mass in a very fine form. It is particularly difficult to develop the grain boundaries in the rolled Al-Mn alloys even after a very strong anneal. Vilella's etch accomplishes this if repeated a number of times with repolishing between each etch. Fig. 48 shows the structure of an annealed forging as revealed by a slight etching. Only the clusters of the aluminum manganese compound are noticeable. A deeper etching reveals the grain boundaries beside these clusters as shown in Fig. 49. There is hardly any pitting around the grainlets of manganese aluminide in the forged metal, and this explains the reason why the aluminum manganese alloy or the "hard aluminum" of the U. S. trade shows more corrosion resistance than other alloys.

#### ALUMINUM ALLOYS WITH NICKEL (Plates 25-26)

Nickel in aluminum also forms an aluminide,  $\text{NiAl}_3$ . This latter shows, however, less tendency to form elongated individual crystals as observed for iron or manganese. In fact its grainlets are quite equiaxial even up to 4% Ni.

Fig. 50 shows the structure of a sand cast alloy with .7% nickel. This case presents practically the only instance of a real eutectic surrounding the grains of primary aluminum. By increasing the amount of nickel the grainlets of the aluminide increase in amount and the structure appears increasingly eutectic. And even far beyond the actual eutectic point of the constitutional diagram the aluminide of nickel doesn't form large crystals in chill cast alloys, remaining in the form of small grains scattered through a mass of aluminum (Fig. 51). Here is the reason why plain Al-Ni alloys retain enough ductility even at 10% Ni.

Plate 26 represents a chill cast alloy with 1.5% nickel and .7% iron. Both aluminides form a fine eutectic network around the primary crystals of aluminum. A slight coring is

Starting from pure aluminum, *i.e.* with less than .2% iron and adding more and more silicon one usually finds the latter scattered in roughly eutectical patches around the fields occupied by primary aluminum and this continues until 10.5% Si is reached. At this point we have the eutectic as determined by thermic analysis.

Fig. 58 shows the structure of this eutectic alloy. With a magnification anywhere above 50 d. one finds but little of an eutectical structure in the alloy. Each particle of silicon has a substantial size and a very definite shape and is imbedded in aluminum all around. However, no more well-defined aggregates of aluminum metal being present in the alloy justifies its definition as an eutectic.

By treating the same alloy with a very small amount of sodium the whole structure is changed. The grains of silicon become less angular, much smaller in size and much more concentrated. In the case of a 10.5% Si alloy one obtains a definite eutectic which surrounds islets of primary aluminum, as shown in Fig. 59. This last picture was purposely taken from an alloy, that was not kept long enough under the influence of the refining process; that is why the grainlets of silicon are still of a substantial size and quite individualized.

Figs. 60 and 61 show the structure of an identical alloy but prepared from aluminum purposely contaminated with .4% iron. The general appearance of the grainlets of silicon is about the same as in Fig. 58; they are, however, much lighter colored, and, among them, radiating in every direction, lie the dark-colored long needles of the X constituent. These needles become still more pronounced (though the outlines are finer) in the same alloy upon treatment with sodium. In this case the pouring was delayed long enough and the refinement of the grainlets of silicon went beyond that shown in Fig. 59. The islets of aluminum in correspondence to the shifting of the eutectic to the silicon side have acquired definite outlines.

Fig. 62 shows the structure of a commercial casting executed in the silumin alloy containing 1.05% iron. The amount

of the X constituent is large but not excessive and its individual needles quite small.

In Fig. 63 an alloy is represented, which was prepared under adverse conditions, about 1.65% Fe entering in the melt. The needles of X are exceedingly large. Their long edges are colored dark violet.

Figs. 64 and 65 show the structures of the same two castings at 250 d. That the differences in the sizes of the silicon grainlets are due to the variation of the iron content is quite apparent. The needles of X reveal by a darker coloration of discontinuous strips covering in parts their edges the existence of a reaction between a silicon-rich central stem and the iron aluminide that concentrates at the surface.

Plate 33 reproduces the macrostructural features of aluminum silicon alloys of nearly the exact (10.5%) eutectic composition. In Fig. 66 corresponding to the microstructure of Fig. 58 each individual crystallization pocket shows a grayish core (eutectic) and a light rim. In spots, these pockets are very large but ill defined and show a light dendritic core of excess aluminum.

Fig. 67 pertains to the same composition but modified by sodium treatment (see Fig. 59). The crystallization pockets are much more uniform and more sharply outlined. The sharp white lines at their boundaries are due to the excess aluminum.

Fig. 68 on the other hand shows the alloy not only lacking the modifying treatment but in addition contaminated with iron. Grayish boundaries and white cores mark the primary pockets replacing the opposite shades of the finer alloy. Pinholes become abundant and occur mainly within the white cores. The purer alloy is practically clean from them in both cases described.

The same alloy after the modifying treatment (see also Fig. 61) still retains light cores and dark boundaries (Fig. 69). The crystallization pockets are much larger. The number of pinholes is nearly the same.

Fig. 70a shows a cross section of a casting made of a high

iron silumin (9.3% Si, 1.65% Fe) in the unetched state. It contains plenty of pinholes and large needles of X. Fig. 7db represents the same as etched by the method of Flick. The crystallization pockets are large and ill defined.

Fig. 7oc shows a fracture of the same casting. It looks roughly crystalline. The visible crystals are, however, nothing else than the primary crystallization pockets separated from each other due to the brittleness of the long needles of the X constituent located between the pockets.

Figs. 71 and 72 represent the structural changes taking place in both the high iron and the moderately contaminated castings on remelting and solidifying in vacuo. In both cases the absence of air seems to have had a refining action upon the grainlets of silicon, the islets of aluminum also getting better defined. No segregation whatsoever takes place due to slow cooling. Needles of X become much larger, better defined and darker in both cases. It looks, however, as if even in this case the reaction giving birth to the X needles did not yet reach the state of equilibrium. In both cases the vacuum melting and solidifying lead to a complete absence of pinholes.

Fig. 74 shows that sodium treatment applied to a high iron alloy affects only the size of the silicon grainlets and the space occupied by the modified eutectic. There is no visible effect upon the needles of X.

Figs. 74 and 75 show the structures of a sand cast 12.5% silicon alloy (about 0.6% Fe) in the plain and the modified state. The main features are: the disappearance of primary silicon grainlets and the formation of a true eutectic structure due to the sodium treatment.

In Figs. 76 and 77 one perceives the influence of both chill casting and sodium treatment upon the structure of the 12.5% Si alloy. Even without the special treatment the chill cast structure is similar to that of the same alloy when sodium treated and sand cast. The combination of chill casting and the modifying process leads to a further progress in the refinement of structure.

Figs. 78 and 79 show the differences in the structures of the modified alloy due to the type of the mold (chills against sand). In the latter case not only are the silicon grainlets many times larger, but the X needles are also far stronger developed. In the chill cast state their formation is almost entirely suppressed.

Plate 39 is intended to show the importance of macrostructural examination in the case of the "Alpax" type alloys. Fig. 80 shows the type of unsoundness frequent in this alloy if not modified. Fig. 81 pertaining to the same casting in the etched state shows the lack of uniformity in the primary crystallization pockets. Fig. 82 demonstrates the results of a sodium treatment which was allowed to proceed to completion. The central part consists of a less refined metal and corrodes more, *i.e.* etches much darker than the fully modified outside layer.

#### ALUMINUM ALLOYS WITH COPPER (Plates 40-57)

Figs. 83 and 84 show the structures of a very pure *sand cast* Al-Cu alloy (3% Cu, 0.2% Fe). Fig. 83 pertains to the raw alloy and shows cored grains of a very variable size with fine elongated crystals of  $\text{CuAl}_2$  within the dark shaded rims of the grains. In Fig. 84, taken after an annealing for 20 hours at  $500^\circ$  and air cooling, the cores are completely gone and the alloy represents a perfect solid solution with large polyhedral grains. Old crystallization pockets are still recognizable by the uniform shade of the groups of new grains previously forming their parts.

Plate 41 shows the cored structures of practically the same alloy but contaminated with 0.8% iron and *chill cast*. Due to a largely suppressed equilibrium, the grainlets of  $\text{CuAl}_2$  (pinkish white) are more pronounced in amount. The iron aluminide is concentrated in spots (Fig. 86) and forms clusters of black (dark violet) particles frequently resembling the "Chinese Scripts."

The same alloy in the forged and thoroughly annealed state is represented by Figs. 87 and 88. They illustrate mainly the

crystalline structure of the alloy and also the manner in which the iron-aluminide is distributed.

Figs. 89 and 90 illustrate the structure of a sand cast 5% Cu alloy also practically free from iron. The crystallization pockets in this case are very large and show plenty of cores. The excess copper aluminide forms large aggregates within the dark belts (Fig. 89). The same alloy when annealed at  $450^{\circ}$  and quenched forms a mass of large sized homogeneous crystals, all excess of  $\text{CuAl}_2$  having disappeared by diffusion into the adjacent grains (Fig. 90).

Same alloy annealed at  $520^{\circ}$  and quenched shows an entirely different structure (Fig. 91). This temperature being slightly above the solidus point of the alloy the excess of  $\text{CuAl}_2$  oozes out from the old grains. On cooling it produces new boundaries and makes the new grains smaller.

Fig. 92 shows the same alloy as hot forged. The boundaries of the old grains became blurred and new smaller grains are developing in the process of recrystallization. There was not enough time for the metal to recrystallize spontaneously and completely and the structure looks neither uniform nor sharply defined.

Figs. 93 and 94 show the influence of the annealing temperature upon the structure of the 5% Cu alloy in the forged state. Fig. 93 pertains to the effects of a heating at  $520^{\circ}$  for 3 hours and quenching. Very sharply defined uniform grains result from this treatment, but in spots the same effect of the copper aluminide eutectic oozing out and forming globular filigree bodies is noticeable. In Fig. 94 representing the same alloy after heating for 5 h. at  $480^{\circ}$  and air cooling the grains are slightly smaller, but somewhat dull (due to a partial precipitation of the  $\text{CuAl}_2$  on air cooling).

Fig. 95 shows the structure of the forged alloy as quenched from  $520^{\circ}$  and heated for 18 h. at  $125^{\circ}$ . Some grains remain just as sharply defined and clear inside as right after quenching. Others are darkened and slightly mottled indicating the presence of a precipitate.

In Fig. 98 we have (at 500 d.) a spot representing a

sharply outlined corner between three grains where a globular filigree mass of the eutectic ( $\text{CuAl}_2 + \text{Al}$ ), supposedly melted during the high temperature treatment and solidified on quenching, is present.

Figs. 97 and 98 show the same alloy as heat treated at  $480^\circ$ , quenched and once again heat treated at  $180^\circ$  for 3 hours. The old grains combine into fields of an identical state of precipitation throughout the alloy. The presence of the precipitate is definitely established.

#### ALLOY N° 12 (8% COPPER, 0.8% Fe) (Plates 48-53)

Increasing the amount of copper one comes to the alloy N° 12 with 8% copper. Figs. 99 and 100 show the macrostructure of this alloy in its sand cast state. One sample was poured at  $850^\circ$  another at  $700^\circ$ . The difference in the size of the primary pockets in the two cases is very clear. Two special conclusions may be reached by examining these macrographs and comparing the physical properties of the cast metal. One — that the very substantial difference in properties resulting from pouring at high and low temperatures does not imply a great difference in the grain size in the "12" alloy. Second — that the presence of large amounts of copper compels the liquid alloy to form primary pockets of a rather uniform size and acts suppressingly upon the crystallization of iron aluminide. In fact with the amount of iron present in these two cases (0.8%) a plain aluminum casting would be entirely structureless.

Plates 49 and 50 are intended to illustrate the comparative value of the micro examination in, (1) the non-etched state, and as etched, (2) with  $\text{HCl} + \text{HF}$  (method of Flick), (3) with sodium hydroxide, and (4) by the nitric acid quench. Two specimens of castings in alloy N° 12 as poured at the normal ( $700^\circ$ ) and at a too high temperature ( $850^\circ$ ) were used as examples. The only appreciable difference consists in the strength of the darkening wrought upon the  $\text{CuAl}_2$  particles and filigrees by various etches.



• Figs. 109-110 show the same alloy as cast at 700 and 850°, examined after the etching with Vilella's reagent. In Fig. 109 due to the slowness of the cooling the equilibrium is more nearly reached. The white cores are large, their rims narrow though very dark and within these rims only a little of the excessive  $\text{CuAl}_2$  is found. In Fig. 110, the rims of the grains are larger, and within them one notices white chains of copper aluminide and dark clusters of iron aluminide.

Figs. 111, 112, 113 and 114 give the idea of the structure of the same alloy in the chill cast state, the pouring being done at various temperatures. The latter fact is strongly reflected in the variation of the coring, the size and amount of copper aluminide and particularly in the form of the iron aluminide.

Figs. 115 and 116 show the structure of an auxiliary alloy with 40% Cu. Almost 85% of the total space is occupied by the  $\text{Al}-\text{Al}_2\text{Cu}$  eutectic. Imbedded in its mass are dark particles of  $\text{FeAl}_3$  and long black needles of the X constituent.

Figs. 117-120 represent the structure of a piston alloy containing 12% Cu, 2% Mn and 0.8% Fe. The effects of a light and a dark etch are shown in this case.  $\text{CuAl}_2$  appears as white filigrees within the rims of the core grains. Inside the light cores a number of gray or black (dark violet) crystals, reminding one of arrowheads, occurs. They represent most probably a double aluminide of Mn and Fe. At high magnification one finds the grains of  $\text{CuAl}_2$  to be associated with the X needles.

Fig. 121 represents another piston alloy used in the heat treated state and developed by S. Daniels of the U. S. Air Service. A large number of micrographs of this composition in various states may be found in the "Forging, Stamping, Heat Treating for 1925, p. 346, and in the Tr. Am. Inst. M. & M. Engrs., 1926). Our picture is intended to give the idea of the coring and the distribution of the  $\text{CuAl}_2$  (light gray) and  $\text{FeAl}_3$  (dark violet) in the alloy as cast.

**COMPLEX ALLOYS CONTAINING COPPER AND SILICON . .**

(Plates 58-65)

Figs. 123 and 124 represent the Lantal (4% Cu·2% Si in general + 0.6% Fe in this particular case) alloy in the chill and sand cast states. The influence of the method of casting upon the grain size, amount of coring and the development of the grainlets of Si,  $\text{CuAl}_2$  and the needles of X is very clear.

Figs. 125 and 126 show the structure of two different spots in the sand cast alloy at a higher magnification. In Fig. 125 there is very little free silicon but plenty of the X needles. In Fig. 126 one sees a few larger grainlets of silicon and the "Chinese Script" phase of  $\text{Al}_3\text{Fe}$  among them.

Figs. 127-129 represent the same in the forged state. Fig. 127 shows the results of quenching from 480° and Fig. 128 after 12 h. treatment and a subsequent heat treatment at 250° (intentionally excessively high for the sake of causing a visible precipitate). Fig. 129 pertains to the same state as Fig. 128 but shows it at a higher magnification. The boundaries developed in the heat treated metal are now bright, the precipitate concentrating more at the core of the grains. Silicon and  $\text{FeAl}_3$  are scattered mostly at the grain boundaries but appear to an extent also within the grains.

Figs. 131 and 132 represent the macrostructures of another ternary alloy which we are going to call the "Dix" alloy (3% Cu and 5% Si). In the chill cast state the crystallization is influenced by the copper and the primary pockets are clear cut (slightly blurred toward the center) and equiaxial. In the sand cast state the influence of iron and particularly of the X predominates and the whole aspect of the crystalline conglomerate becomes entirely different.

Figs. 133-138 show the microstructure of the Dix alloy. Figs. 133 and 134 illustrate mainly the influence of the method of casting upon the grain size. Figs. 135 and 136 show the structures of the eutectic patches, the size and appearance of the X needles. In the sand cast state the latter are much larger, gray of shade and straight. In the chill cast form they appear much finer and colored a dark violet (on etching).

Figs. 137 and 138 show the changes in the structure of the same sand cast alloy caused by a heat treatment for 20 h. at 480°. Coring has entirely disappeared. Needles of X became smaller and darker colored. The eutectic particles of silicon coagulated to a large extent.

#### ALUMINUM ALLOYS WITH ZINC (Plates 66-72)

Zinc is another element which forms solid solutions with aluminum.

Figs. 139 and 140 show the structure of a solid solution alloy of 5% Zn with the purest commercial aluminum, both as sand cast and as annealed.

In Figs. 141-144 is represented the structure of an aluminum-zinc alloy, containing 15% Zn and according to the constitutional diagram forming a perfect solid solution. In the chill cast state it shows a coring opposite in character to that found in Al-Cu alloys. Here the core is dark and the rim of the grain is light. The grain boundaries are made up usually of eutectically looking patches consisting of the  $\text{Al}_2\text{Zn}_3$  compound and its dissociation products (finely distributed particles of zinc). In the case illustrated, the grain boundaries carry also the  $\text{FeAl}_3$  compound in the form of sharp edged gray crystals. The X constituent is absent.

An anneal at 470° followed by quenching eliminates coring and brings out the grain boundaries in a sharp manner (Fig. 43). The  $\text{FeAl}_3$  becomes finely dispersed within the newly formed grains. Forged and subjected to the same heat treatment the alloy develops a definitely crystalline structure, somewhat blurred, due to the unevenly accumulated  $\text{FeAl}_3$  (Fig. 144).

Figs. 145-152 represent the structures of the 2:1 alloy (33% Zn) in the cast state, both with and without a subsequent heat treatment. In Figs. 145 and 146 the difference between the grain size in the chill and the sand cast state is recorded. An interesting feature of the sand cast alloy is the double coring of the grains, the finely traced grain boundaries, and the peculiar distribution of the iron-aluminide.

The structural differences of the two forms of the cast alloy are still clearer in Figs. 147 and 148, where they are shown at high magnification. The average grain size of the sand cast alloy seems to be at least four times larger in area than that of the chill cast one in spite of the magnification being twice lower (250 d. against 500).

A heat treatment at  $410^{\circ}$  for 10 hours eliminates the coring completely and straightens the grain boundaries in both cases (Figs. 149 and 150). The  $\text{FeAl}_3$  in the case of the chill cast alloy agglomerates into large gray particles while in the sand cast it forms large dark clusters.

Fig. 151 represents the chill cast, heat treated, and quenched alloy after an ageing lasting for six months. The large grains became incompletely broken up into smaller crystals and the surface looks in spots quite foggy, probably due to a fine precipitation of zinc.

Fig. 152 pertains to the alloy that was subjected to an additional heat treatment with the aim of accelerating the ageing process. The metal becomes so sensitive to corrosion, that even a very short immersion in any etching medium covers the whole surface with a dirty film consisting, most probably, of the zinc that precipitated from the solid solution on heat treating. Only a few faint outlines of the old grain boundaries remain visible (light lines) and the only bright specks in the whole surface are due to clusters of iron aluminide which seem to be free from the film.

**THE GERMAN ALLOY (12% Zn, 3% Cu + 0.7% Fe)**  
(Plates 73-75)

The next group of photomicrographs illustrates the effects of various etching methods upon the development of the structure in the sand cast German alloy (12% Zn and 3% Cu) and the structural variations due to the type of the mold and the temperature of pouring. Of the previously known etching media sodium hydroxide seems to yield more detail (differentiation between the gray  $\text{CuAl}_2$  and the dark  $\text{FeAl}_3$ ). The use of Vilella's etch adds grain boundaries and the coring

within the grain, to the features mentioned (Fig. 157). The shape in which the  $\text{CuAl}_2$  occurs is illustrated clearly in Fig. 158 at 500 d.

Fig. 122 (Plate 57 shows an interesting case of the occurrence of Chinese Script in the sand cast alloy.

#### ALUMINUM ALLOYS WITH TIN (Plate 76)

The problem of the structure of Al-Sn alloys is still far from a complete solution. It is usually believed, that at least 10 and perhaps 20% of tin go into solid solution (see Gulliver's "Metallic alloys").

Fig. 161 shows that at least for a sand cast alloy with 5% Sn, this assumption does not hold. In this case a large part of the tin is present at the grain boundaries in the form of a continuous thick film. Had this excess tin been due to imperfect diffusion, the inside of each grain ought to present a cored appearance. This, however, is not the case and instead of coring one finds a definite secondary constituent in the shape of a fine precipitate and a number of small round grainlets of tin entrapped during the crystallization.

The same alloy is represented in Fig. 162 in the heat treated (500°) and *quenched* state. The excess of tin has largely disappeared. The grain boundaries however are not uniform. In spots they are very wide and uneven. They seem to contain some foreign substance which probably consists of films of aluminum or tin oxides.

Alloys higher in tin etch badly. It has been almost impossible to ascertain the exact nature of the intergranular substance present in the cast state. The only point established is that, with and above 8% tin not even a nearly complete homogenization can be reached.

#### ALUMINUM ALLOYS WITH MAGNESIUM

(Plates 76-78)

Our knowledge of the structural relations in this system was not yet obtained in a direct way, but has been practically without exception deduced from the data of the thermic analy-

sis. The literature of the subject is full of micrographs which are either too inferior to be discussed, or relate to alloys way beyond the supposed solid solution range.

Micrographs described in the following are also far from the desired clearness and hardly lend themselves to interpretation. Figs. 163 and 164 for instance show the structure of a 5% Mg alloy which was only slightly contaminated with iron 0.4%. From the standpoint of the constitutional diagram it should have represented a solid solution with very little if any of the  $Al_3Mg_2$  compound crystallizing at the grain boundaries. The grains themselves ought to be definitely cored.

Nothing of this kind is seen in Fig. 163 at 100 d. or in Figs. 164 at 500 d. The area under examination is full of chainlets of a dark mass, which escapes identification.

Forging followed by heat treatment ( $500^{\circ}$ ) and quenching ought theoretically to bring all magnesium into a solid solution and produce a recrystallization usual in aluminum alloys. Fig. 166 presents a faint resemblance to a recrystallized alloy, but practically no grain possesses a closed boundary, and even those boundaries which seem to have been developed are rather thick and remind one more of a film of oxide, than of the regular edges of metallic crystals. In Fig. 165, which represents another spot in the same sample, not even a trace of a grain boundary is seen, while the amount of the secondary constituent of a gray shade is too large to correspond to the iron present in the alloy to which according to the usual presumptions and customs, all undefinable structural elements are ascribed. Experiments with an alloy of the same magnesium content but almost free from iron did not lead to better results. The alloy in the forged, heat treated ( $470^{\circ}$ ) and quenched state is represented by Fig. 167 and 168. Once more no definite grain boundaries are visible; on the contrary one sees a great deal of eutectically looking patches, containing some secondary constituent. The eutectic as shown in Fig. 168 at 500 d. does not lend itself to a theoretical elucidation. The raw materials contained only traces of silicon and

therefore the secondary constituent of the eutectic can by no means represent the compound  $\text{Mg}_2\text{Si}$ . To regard it as forming that second phase of the Al-Mg series, which has for its base the compound  $\text{Mg}_2\text{Al}_3$ , would mean a definite denial of the supposedly large range of solid solubility of magnesium in aluminum.

Papers by Flick (Tr. A.I.M. & M. E., V. 71, p. 816), Hanson and Archbutt (J. Inst. Metals, V. 21, 1919) and S. Daniels (J. Ind. Eng. Chem., V. 16, 1924, p. 1243) also reproduce structures of Al-Mg alloys and mostly within the supposed range of solid solutions. None of their illustrations can be considered as presenting a proof of the general contention that 6% at least and probably up to 12% of magnesium go into solid solution in aluminum. To resume: The present technique of micrographical investigations of aluminum magnesium alloys of low Mg. contents has not yet reached the stage where grain boundaries or coring can be ascertained, and this fact taken together with the constant presence of an eutectical structural element leaves the question of the structure of aluminum magnesium alloys fully open.

It is of importance to mention at this point, that efforts to obtain clean buttons of Al-Mg alloys by remelting the latter in a high vacuum do not lead to positive results, the individual pieces or chips refusing to run together even at temperatures above  $800^\circ$ .

Figs. 169 and 17b relate to an alloy containing 18% magnesium and contaminated with 0.8% Fe (from the raw aluminum ingot). Alloys of this content are used as auxiliary materials in the manufacture of duralumin and analogous compositions.

According to the constitutional diagram the structure of this alloy ought to represent isolated islands of the (Al-Mg) solid solution imbedded in an eutectic formed of the same solid solution plus the nearest compound ( $\text{Mg}_2\text{Al}_3$ ). Fig. 170' shows plainly that no such eutectic is formed. On the contrary the alloy consists of a white ground mass and a gray constituent occupying at least 40% of the space. The structure reminds

.. one more of 10% aluminum bronzes or 40% zinc brasses, where one constituent (alpha) is formed by a continuous transformation from the one which crystallized primarily (beta). This discrepancy between the results of the thermic studies and the visible structure once more proves that the Al-Mg alloys are still far from being sufficiently well studied.

#### ALUMINUM ALLOYS WITH MAGNESIUM SILICIDE

(Plates 81-85)

As explained in chapters dealing with ternary systems the case of the simultaneous presence of magnesium and silicon belongs to those few ones where one secondary element (silicon) is able to tear away from aluminum the other secondary element (magnesium) with which the aluminum is combined. Fig. 171 illustrates this case, the example being that of an alloy containing nearly 20%  $Mg_2Si$ . The eutectic in the system, aluminum — magnesium-silicide, is supposed to lie at 12%  $Mg_2Si$  and in the case under consideration nearly 8% of this compound must crystallize in the form of primary crystals. This actually happens and the micrograph in Fig. 171 contains approximately this amount of large grayish blue crystals. Their shape looks more or less like that of a crystal belonging to the cubic system which is, however, hardly possible for a substance of a formula like that of  $Mg_2Si$ .

The crystals of magnesium silicide are imbedded in a much lighter mass, consisting of large patches of aluminum and a fine filigree eutectic. Black (dark violet) specks of the iron aluminide are here much more definitely crystalline and equiaxial, than in plain aluminum, due to the coalescing action of magnesium.

By decreasing the amount of magnesium silicide present we come to alloys forming the base of the English "aludur" alloy and the American "51S" both of which represent simplified types of duralumin. The structure of a chill cast billet of aludur is represented in Fig. 172 for the purest alloy and in Fig. 173 for one contaminated with 0.8% Fe. In the first case definite grain boundaries are visible with fine grainlets



of  $Mg_2Si$ , precipitated introgranularly from the primary pockets on cooling, and forming long parallel chainlets. In the second case the  $Mg_2Si$  becomes associated with  $Al_3Fe$  and the granular structure of the alloy is obliterated in the same way as in plain aluminum heavily contaminated with iron.

Figs. 174 and 175 represent the purest aludur ingot as heat treated. In Fig. 174 the treatment (12 h. at  $500^\circ$  + water quenching) served to homogenize the alloy and to make the boundaries of the large primary pockets more clear cut. In Fig. 175 the alloy was additionally treated for 3 h. at  $180^\circ$ . This point is somewhat beyond the temperature used in the artificial hardening of this alloy and was resorted to for the purpose of making the intracrystalline precipitate of  $Mg_2Si$  visible. In fact the etching renders the sections of the grains dull and the former grain boundaries stand out bright from a dark grayish field.

Analogous conditions of heat treatment are represented in Figs. 176 and 177 for the same alloy in the forged state. In the first, one sees sharply defined crystals of a preserved solid solution, while in the second the grains are blurred with the precipitate.

The less clean and more commercial type of the same alloy is represented further in Figs. 178-180. It is the same alloy as shown in the chill cast state in Fig. 173. As homogenized by heat treatment and quenching it is shown in Fig. 198. The field is clear, but no grain boundaries are visible. The presence of short rods of the X constituent compels all etching action to concentrate at their edges and prevents the crystal boundaries from becoming developed.

The same holds true for the forged alloy in the homogenized state (Fig. 179). After the second heat treatment, however, the grain boundaries are seen as light lines in a field blurred by the  $Mg_2Si$  precipitate (Fig. 180).

THE MACROSTRUCTURAL INFLUENCES OF VARIOUS  
STRUCTURAL ELEMENTS (Plates 86-88)

With the description of the simpler cases of aluminum alloy structures completed, it becomes of interest to summarize the macrostructural influences of various elements if present separately or simultaneously.

That iron, if present alone, quickly leads to a suppression of the crystal-growth in the process of the solidification of aluminum has frequently been stated in the preceding. That copper and zinc counteract this action and produce uniformly sized primary pockets was also outlined in the discussion of the structures of binary systems. In the following a presentation will be given of the influences wielded by these and other elements both in the sand cast and chill cast states.

(a). The Sand Cast State. Aluminum Ingot of 99.7% Purity

Fig. 181 shows the influence of 3% copper upon sand cast aluminum (compare with Fig. 6). The primary pockets are much more uniform. Etching leaves the various surfaces of the primary pockets smooth and flat. The reflection of light is decidedly sharp and the pocket boundaries become therefore quite definite.

Fig. 182 shows the influence of 5% zinc. Primary pockets are very uniform in size. Their surfaces are, however, much less brilliant.

Fig. 183 shows the influence of 4% silver. Primary pockets are reduced in size much more than in the first two cases. Pocket boundaries are sharp; their surfaces, however, not so smooth, traces of a further subdivision due to the formation of internal eutectical chains of  $\text{Ag}_2\text{Al}_3$  being clearly visible.

Fig. 184 shows same alloy after prolonged anneal at  $480^\circ$  (24 h.). Pockets are larger, sharply defined and more smooth.

Fig. 185 shows the influence of 2% manganese. The size of the primary pocket is decreased to nearly the same degree as due to 3% of copper. The pockets are, however, dull and

ill defined. No selective etching action along definite planes takes place, the intergranular crystallization of the  $MnAl_3$  preventing it. However, this preventive action is much less strong than that of 0.6% of iron.

Fig. 186 shows the influence of 2% magnesium. This is very much like that of zinc, but the size of the primary pocket is decreased more by 2% Mg than by 5% Zn. At 4% Mg the primary pockets are not visible any more.

Fig. 187 shows the influence of 2% tin. The size of the primary pockets is less affected than by 5% zinc; their surfaces are, however, quite dull (compare with Fig. 185, i.e. the influence of 2% Mn).

Fig. 188. Five per cent of tin affects the macrostructure almost exactly like 2% magnesium.

**(b). The Chill Cast State (All Alloys Contain Nearly 0.7% Fe)**

Fig. 189, 5% Cu shows sharply defined primary pockets.

Fig. 190, 2% Mn shows visible primary pockets.

Fig. 191, 15% Zn shows primary pockets much smaller but rather clear.

Fig. 192, 5% Mg shows no primary pockets to be visible.

Fig. 193, Duralumin. In spite of the presence of iron, manganese and magnesium the 4% copper makes a strong development of primary pockets possible. The macrostructure is very much like that of an aluminum ingot contaminated with 0.6% iron.

Fig. 196, Magnalite (Y alloy). The same action of copper making the primary crystallization more definite takes place in spite of the presence of iron and a high content of nickel (2%) and magnesium (1.5%), both of which tend to reduce the size of the primary pockets.

The action of chill casting at various temperatures is shown in plate 88 for  $\frac{1}{2}$ " thick plates of the two commonly used alloys, "N° 12" and "German." In the first one when cast at a high temperature (some 250° above the full melting point) the tendency is to form columnar crystals (like in aluminum metal billets). At the normal temperature the pockets are

equiaxial but still sharply defined. With the second alloy a casting at a high temperature produces uniform pockets, while at a low temperature the primary pockets become almost indiscernible.

**DURALUMIN:** (4.0% Cu, 0.5% Mn, 0.5% Mg, 0.7% Fe)

(Plates 89-102)

Alloys of the duralumin type are always complex from the standpoint of chemical composition and physical nature. That is why an elaborate structurographical study is of the highest importance in this case. Unfortunately the methods of preparing the specimens and etching them were not sufficiently well developed in the past, and accordingly there is hardly one illustration of the structure of duralumin among all those which appeared from time to time in various publications that is of much value for this purpose. Figs. 199 and 200 taken at 100 d. represent the results of polishing and etching with sodium hydroxide as was usual a few years ago and obtained by the author on a past occasion. The micrograph of the chill cast state (Fig. 199) represents nothing but a mass of tiny dark specks, shapeless and of no definite shade. In Fig. 200 for the sand cast state one sees grayish and black specks, still entirely shapeless and located in the utmost disorder. It is impossible to tell in both cases either the grain size or how chemically inhomogeneous the grains are.

An entirely different picture can be obtained from Figs. 201 and 202 relating to exactly the same samples of the alloy when the new (Vilellais) etch was applied. In Fig. 201 one may establish the size of the grains definitely and one sees also that the grains are cored, their thin rims being rather dark. The secondary constituents are too small of size to be seen at this magnification. In Fig. 202 the same alloy is represented in the sand cast state and it is just as well possible to appraise the size of the grain and to see that the grains are largely cored. Within their grayish rims white specks of an irregular shape represent the excess of copper aluminide while

the blackish specks, mostly confined to the dark rims, though frequently appearing within the grains also, represent the iron and probably manganese aluminide.

The sand cast structures are studied in more detail in the next eight photomicrographs. Fig. 203 shows a spot where the grayish-looking grainlets of copper aluminide and the black sharp crystals of iron aluminide imbedded in the grayish rim of the individual grain form the main feature of the alloys. In Fig. 204 a lone spot is shown where the iron aluminide forms a very interesting type of the Chinese Script. One may note that not a grainlet of copper aluminide is present anywhere in the neighborhood.

Figs. 205 and 206 show the same alloy as annealed for 10 hours at  $500^{\circ}$  and quenched. All coring disappeared but the excess of the bright copper aluminide is seen all around. The particles of iron and manganese aluminides did not change much, but became somewhat rounded.

Figs. 207 and 208 relate to the same alloy but additionally treated for two hours at  $150^{\circ}$  after the quenching. At a magnification of 100 d. one sees the differently shaded primary pockets subdivided into smaller oval grains. Some pockets contain a large amount of precipitate while others remain much brighter. At a higher magnification one can notice the precipitate in the grains, the bright filigrees of the excess of copper aluminide and black specks of iron and manganese aluminides.

Figs. 209 and 210 relate to the same alloy heated at  $200^{\circ}$  instead of  $150^{\circ}$  for the same amount of time. The precipitate is more plainly visible and more uniformly distributed through the whole mass of the alloy.

The next group of illustrations relate to the chill cast state. Figs. 211 and 212 represent structures of the same specimen as shown previously in Fig. 199 at a lower magnification. In Fig. 211 the alloy is built of grains of a smaller size than those in Fig. 212 and the coring is more pronounced. The excess copper aluminide within the gray rims of the grains is rather dark. There is in general no separation of

the iron aluminide from copper aluminide. Only in a few spots at the corner of the bar the small oval specks of copper aluminide crystallize separately and appear bright.

In Fig. 213 the same alloy is shown as quenched after 10 hours at  $500^{\circ}$ . All coring disappeared but the excess of the copper aluminide (if present) is not separated from the iron aluminide. In Fig. 214 the same alloy is shown after an additional treatment for three hours at  $220^{\circ}$ . It carries an unmistakable precipitate.

Figs. 215 and 216 relate to the same chill cast alloy after it had been quenched from  $515^{\circ}$ . For reasons which cannot yet be definitely explained the chill cast alloy doesn't stand a treatment at this temperature contrary to the behavior of the sand cast and the rolled alloys. One sees that the whole alloy recrystallized forming much larger grains with finer boundaries. The latter are, however, either enlarged or discontinued in spots by the appearance of a thick filigree of a copper aluminide containing the eutectic which oozed out from the grains during the treatment at  $515^{\circ}$ . A great deal of copper aluminide also coagulated within the grains. It is of interest that in no spot is the copper aluminide as bright as it appears in the sand cast state. There is a probability that in this case copper aluminide forms a double compound with other aluminides and so acquires the property to etch dark.

Figs. 217 and 218 represent the same alloy as in the last two illustrations but treated for two hours at  $320^{\circ}$ . All grains are now full of precipitate. The grain boundaries are bright and the filigrees of the excess copper aluminide almost disappeared (probably due to diffusion).

Figs. 219 to 222 represent a forged bar of the same duralumin composition as stated above. In Fig. 219 one sees it as quenched after one hour at  $500^{\circ}$ . The field shows promiscuously distributed grainlets of iron and manganese aluminide or their double compound and nothing else. In Figs. 220 and 221 the same is shown after a subsequent treatment at  $150^{\circ}$ . The previously bright ground mass became cloudy due to the precipitate. In Fig. 222 the same alloy is shown as air cooled

and having developed a slight amount of a precipitate which is however confined to a few spots only.

Figs. 223 and 224 represent the structures of the same duralumin after it was heat treated at  $500^{\circ}$  for 10 hours and had accordingly enough time to recrystallize. Both the grains of the ground mass and the crystals of the aluminides of iron and manganese are clearly visible.

In Fig. 225 the same bar is shown after a treatment for 2 hours at  $150^{\circ}$ . The grain boundaries have lost in definition and a faint precipitate is seen all around the black particles of the aluminides.

#### ALLOYS CONTAINING NICKEL AND COPPER SIMULTANEOUSLY (Plates 103-105)

A simultaneous addition of copper and nickel with or without magnesium is often practiced at the present time. Therefore the structures of such alloys undoubtedly require a more intimate study.

Figs. 226 and 227 represent the structures of an alloy containing 2.3% copper and 2.5% nickel in the sand cast state. The presence of nickel leads always to the appearance of fine fan-like distributed rods, of a compound which may represent either the individual nickel aluminide or more probably a double aluminide of nickel and copper,  $\text{CuNiAl}_3$ . In spots one sees filigrees of the copper aluminide and black particles of iron aluminide. In this case, however, the alloy was made of practically pure aluminum, and iron is almost absent.

Higher amounts of nickel (3.7%) and of copper (4.0%) lead to structures represented in Figs. 228 and 229a-b. The latter are not very uniform. In spots one perceives a dense mass of eutectic-looking bands while between them the space is much brighter and carries only finely dispersed eutectical patches. However, in no place is the structure large grained enough to permit the identification of the copper and nickel aluminides and their binary compounds.

In Figs. 230 and 231 one sees an alloy with still higher

amounts of nickel (4.8%) and copper (4.3%). Nickel appears here in the form of long needle-like crystals frequently distributed in the form of hexagonal stars. In many spots one sees the nickel aluminide in the form of an eutectic with a central axis and fine needles radiating from it. In other places one sees the grayish double compounds and the whitish grains of copper aluminide. The latter appear mostly within the dark rims of the cored grains.

#### MAGNALITE (Plates 106-107)

From the plain ternary alloys one comes to the largely used quaternary alloys containing substantial amounts of magnesium. The most common alloy in this class is the so-called "magnalite" or "Y" alloy. This latter although being rather strong and very important for the present foundry work is likely to produce unsound castings due to the absorption of gases. It was mentioned already in the part dealing with the technology of aluminum alloys that Archbutt developed a method of casting leading to a perfect product. The method entails the freezing of the melt in the crucible, so as to allow the gases to escape, remelting the frozen mass, and pouring at a low temperature. Plate 106 gives a clear presentation of the value of Archbutt's method. Fig. 232 shows a sand casting executed in the regular way and poured at 750°. It is full of pinholes. Fig. 233 is the same casting obtained by the method of Archbutt and there is not one pinhole to be seen. The same is shown in Fig. 234 in the etched state, and the uniformity of the macrostructure leaves nothing to be desired. There was a large amount of iron present in this case and it prevented the formation of visible primary pockets.

Figs. 235 to 238, obtained by the courtesy of S. Daniels of the U. S. Army Air Service, show the structures of the sand cast magnalite alloy as developed by the nitric acid quench. Figs. 235 and 236 illustrate the structure of the cast material and Figs. 237 and 238 that of the quenched and heat treated. One sees the fan-like eutectic containing the double aluminide and the filigree eutectic of the copper aluminide.



Fig. 239 shows the sand cast magnalite at 100 d. as etched by Vilella's method. The long bands of the fan-like eutectic of the double aluminide are located within the elongated individual grains of the alloy. The grains themselves are definitely cored and within their dark rims one sees again the white particles of copper aluminide.

Fig. 240 represents the same alloy in the chill cast state corresponding to the "Y" alloy of Rosenhain. One perceives the comparative smallness of the grains and the fineness of the secondary constituents which form fine chainlets where the individual constituents cannot be distinguished from each other.

The structure of the same sand cast alloy is shown in Figs. 241 and 242 at 500 d. In the first one perceives the particles of copper aluminide, a few elongated grains of the double compound and some needles of the X constituent which are, however, in this case less elongated and broader than in alloys of a less complex nature. In the second figure the fan-like eutectic of the double compound is clearly seen within a large grain with a dark rim and with particles of copper aluminide imbedded in this rim.

Figs. 243 and 244 relate to the same sand cast specimen as Fig. 239 after it was annealed for 10 hours at  $500^{\circ}$  and quenched. The coring disappeared. The fan-like eutectic of the double compound remains unchanged. The iron aluminide coagulated in dark gray masses and the excess of copper aluminide forms either isolated particles or filigrees.

Figs. 245 and 246 represent the same alloy as sand cast, quenched after 10 hours at  $500^{\circ}$  and given a second treatment for two hours at  $220^{\circ}$ . The fan-like eutectic within the grains now etches darker. The copper aluminide is gray and the grains themselves are full of precipitate.

The structures of the chill cast and heat treated Y metal are represented in Figs 247 to 250 as reproduced from the paper by Rosenhain and Archbutt (J. I. M.). The nitric acid quench was used for etching in this case. Figs. 251 and 252 represent the structure of an analogous chill cast bar as

etched by Vilella's method. One sees that the grains are cored. The shape and size of the grains become quite definite and small particles of the secondary constituents are seen at the rims of the grains.

Figs. 253 and 254 represent the same alloy as chill cast, heat treated at  $500^{\circ}$  and quenched. The main new event is the disappearance of the cores and the beginning of development of fine grain boundaries.

Figs. 255 and 256 represent the same alloy as given a second heat treatment after quenching. In Fig. 255 a heat treatment was given at  $225^{\circ}$  and the definite precipitate developed within each individual grain. This precipitate is more concentrated at the center of the grains leaving their rims more or less bright and in this way a definite grain outline is obtained.

In Fig. 256 the drawing was done at  $170^{\circ}$  as usual in the process of heat hardening. The precipitate is too fine to be noticed under these conditions.

The same alloy as forged and quenched after heat treatment at  $500^{\circ}$  is shown in Figs. 257 and 258. In the first the heat treatment lasted for one hour only and the grain boundaries did not become developed. In the second the grain boundaries are definitely developed due to the heat treatment for 10 hours. However, the amount of secondary constituents is so large that they blur the granular structure quite considerably.

Finally, Figs. 259 and 260 represent the structures of the same forged alloy after a double heat treatment and after air cooling from  $470^{\circ}$ . In the first case the field is full of a precipitate and the grain boundaries are practically absent but can be reconstructed from the white patches around the islands of the precipitates. In the air-cooled state one sees only very fine traces of the precipitate and the grain size cannot be identified.



## **APPENDICES**



## APPENDICES

### APPENDIX I

#### *The Aluminum-Boron Series*

It was recently investigated by P. Henri (Comptes Rendus, 1925, v. 181, p. 864). The data gathered by him may be reproduced as follows:

The velocity of the solution of boron in molten aluminum is very low. A prolonged heating of aluminum at  $1400^{\circ}$  C. in a crucible lined with pure boron leads to a product containing 18% boron. The latter is present as needles of  $AlB_2$ .

An auxiliary alloy so prepared dissolves easily in aluminum. Beginning at 1.7% boron an eutectical stop is recorded upon the cooling curves at  $565^{\circ}$  C.

The eutectical point is located at 8.5% boron. The chill cast alloy with 4% boron shows a Brinell hardness of 43, an ultimate strength of 20,000 lbs. per sq. inch and an elongation of 15%. These figures, if corroborated, put the low boron alloys in a decidedly desirable class of alloys.

An addition of 0.3% boron to aluminum copper alloys in the range of 8-12% Cu increases the hardness of the cast metal by 12-20 Brinell units. A desirable strength figure of 23,800 lbs. per sq. inch is also produced.

An addition of 0.3-0.7% boron to alloys containing 13% silicon increases the hardness by 17-22 Brinell units, the ultimate strength by 3000-5500 lbs. per sq. inch and raises the yield point to 9800 lbs. per sq. inch which is decidedly higher than that obtained for the plain or modified aluminum silicon alloys with no boron present.

### APPENDIX 2

#### *The Aluminum Beryllium Series*

Recently great hopes were attached to aluminum beryllium alloys in the development of airplane and airship constructions. In a certain case the idea was propounded, that aluminum beryllium may

have a higher elastic modulus due to the probably higher elastic modulus of pure beryllium.

It is a fact, that the elastic modulus in tension of aluminum (10,000,000 lbs. per sq. in.) is so low, that unless an elastic deformation of over 0.1% is allowed for a structural element made of aluminum, the maximum load carried may not go beyond 10,000 lbs. per sq. in. This is too low a load for a duralumin part with a tensile strength of over 55,000 lbs. per sq. inch.

There is no doubt but that an increase on the elastic modulus to 15,000,000 lbs. would permit a more efficient use of the high strength alloys; still there is very little chance that beryllium might prove of much help. In fact the elastic modulus changes in a strictly additive way for all alloy series containing either solid solutions or eutectics but no compounds. Therefore it might take 16% beryllium to secure the high modulus mentioned, granting that the elastic modulus of beryllium itself amounts to 40,000,000 lbs. per sq. inch which figure may be too high but hardly too low.

The constitutional and physical characteristics of the Al-Be series make such an addition of beryllium well nigh impossible. In fact it is very difficult to introduce more than 2-3% of beryllium in aluminum unless the latter is heated above 1000° C. Even with an auxiliary alloy high in beryllium as can be manufactured electrolytically (reducing beryllium salts with a molten aluminum cathode) the manufacture of alloys as high as 5% beryllium would be beyond the regular foundry practice due to the high temperature required. In addition aluminum-beryllium alloys tend to segregate badly and are apt to be porous.

Only one possibility remains open and bids a fair chance to become an actuality. This is the formation of a beryllium silicide of the formula  $\text{Be}_2\text{Si}$ , which might prove soluble up to 1.5% (0.6% beryllium) in the solid state at the higher and practically insoluble at lower temperatures.

In a case like this the alloy will present a full analogy to the aluminum-magnesium-silicide alloys (aludur) and will yield a material of high strength.

In addition, an excess of beryllium above the amount required by the formula of the silicide will not lead to a chemical sensitiveness of the alloy as is the case of certain duralumin compositions with an excess of magnesium.

## APPENDIX 3

*The Aluminum Lithium Series*

A recent paper by P. Assman (Z. Met-kunde, 1926, p. 51) describes the main features of the aluminum-lithium systems as follows:

Lithium dissolves easily in aluminum metal, but the alloys with more than 10% lithium show no chemical stability whatsoever.

There is an eutectical point between aluminum and a compound of the two metals (possibly  $\text{Al}_3\text{Li}_2$  with 14.5% Li). It is located at the concentration of 7% lithium and at the temperature of  $598^\circ$ .

Alloys containing not over 3.5% lithium solidify as solid solutions and may be preserved in this state by quenching. Alloys with less than 2.2% lithium remain solid solutions constantly.

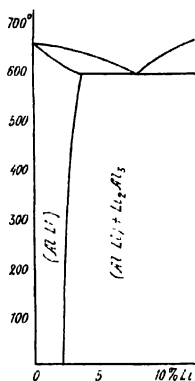


FIG 80 Constitutional diagram of Al-Li alloys by Assmann.

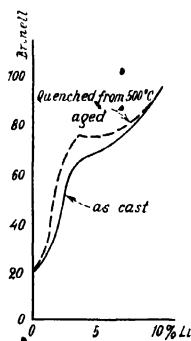


FIG 90 Idealized form of the hardness diagram for Al-Li alloys

The mechanical properties of the binary Al-Li alloys do not seem to be sufficiently known at present to the inventors of the "Scleron" alloys or to Assmann. The latter limits himself to the Brinell hardness figures. The very irregular run of his hardness graphs and the fact that 18 Brinell is taken for the starting point, i.e., the hardness of aluminum, detract from the conclusiveness of Assmann's results. (In fact the hardness of aluminum fluctuates only between 14 and 22 Brinell, according to the conditions of testing and is practically constant for the pure metal provided the ratio of the



load in kg. to the square of the diameter of the ball equals. His figures show that lithium bears a substantially stronger hardening effect than magnesium, and that on quenching iron 525° and ageing all alloys up to 4% lithium become slightly harder than in the raw cast condition.

The effects of the heat treatment and ageing become much more pronounced when either zinc or copper, particularly the latter, are present simultaneously with lithium. An alloy containing 2% Cu and 0.4% Li, *i.e.*, in quantities which taken separately do not respond to heat treatment at all will show 84 Brinell, after being quenched from 500° and aged between 18° and 100°. The same hardness figure can be obtained with 0.4% Li and 12% zinc. However, the latter alloy (according to Tiedemann) may show about the same hardening with a suitable treatment even in the absence of lithium.

To what extent the lithium alloys may prove useful is not possible to predict. It seems however that:—

1. About 0.4% lithium will be required and this will hardly prove cheaper than the 0.5% magnesium used in compositions of the duralumin type.

2. With all useful additions present (4% Cu + Mn or + Ni etc.) the hardness probably will not go beyond 100 Brinell and the strength will hardly amount to more than 50,000 lbs. per sq. inch. (Duralumin of 120 Brinell does not reach above 60,000 lbs.)

## APPENDIX 4

### *The Aluminum-Zinc Series*

The aluminum-zinc series was subjected lately to an original (as to the method used) and substantial reinvestigation within the range of 0-20% zinc by O. Tiedeman (*Z. fuer Met-kunde*, 1926, p. 18). The method devolved upon the study of the ultimate strength and ductility figures for alloys rolled and subjected to a long lasting heat-treatment (from 3 to 11 days) followed by a subsequent quenching. The specimens were tested both immediately and after being aged for 6 weeks. The graphs of the results mentioned as obtained by Tiedeman show no peculiar features from the viewpoint of the previously accepted constitutional diagram (Fig. 55). To the contrary the margins between the properties of the alloys as quenched and as aged which when plotted against the composition

show certain definite tendencies indicative of the more complex nature of the alloys (Fig. 91). Tiedeman and his associates as follows (Fig. 92):

In all alloys under 20% zinc the structure of the alloy immediately after solidification is monophasic just as accepted before. It represents a solid solution of zinc in *alpha* aluminum, and not the monotropic aluminum as formerly accepted.

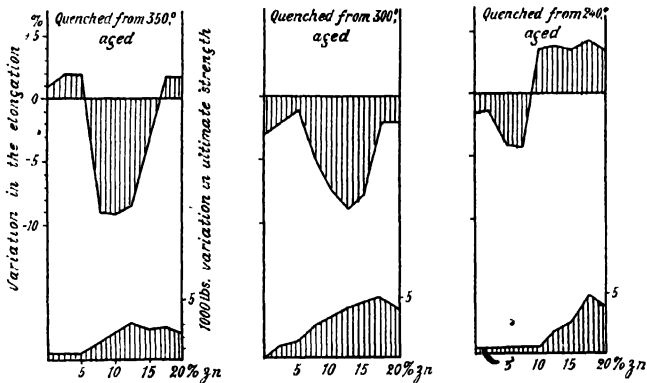


FIG. 91.

Pure *alpha* aluminum is supposed to transform into *beta* aluminum at  $580^{\circ}$ . The presence of zinc lowers this point continuously until a *critical point* of  $275^{\circ}$  is reached at 17% zinc.

Beta aluminum is unable to carry large amounts of zinc in solid solution (just as *alpha* iron cannot carry more than traces of carbon). At  $275^{\circ}$  the saturation limit is found with 6% zinc. It drops, however, to 3% somewhere in the neighborhood of  $120^{\circ}$  and hence remains constant.

At  $275^{\circ}$  *beta* has accordingly an eutectoidal transformation of the *alpha* aluminum-zinc phase and it leads to the precipitation of an aluminum-zinc compound which causes the alloys to harden considerably. Alloys containing between 6% and 20% zinc, if quenched from just below  $275^{\circ}$  are initially built up of *beta* aluminum-zinc crystals plus the mentioned compound in an eutectoidal distribution.

Alloys containing from 3% to 8% zinc remain in the condition just described, while those containing above 7.5% zinc undergo a second transformation during which the aluminum-zinc compound

breaks down and zinc is precipitated. This once more causes a hardening effect.

Alloys containing between 6% and 17% zinc if quenched from above 275° form mixture of alpha and beta aluminum/zinc solid solutions until the compound precipitates in an ultramicroscopical

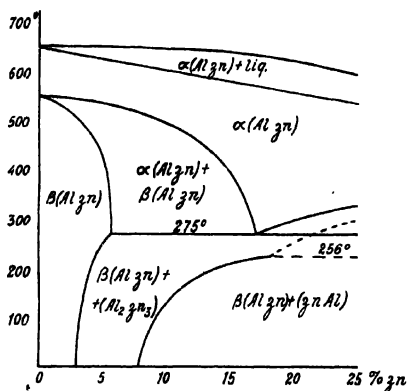


FIG. 92.

form due to ageing. Hence, the maximum hardening effects in the series are obtained.

Tiedeman's conclusions are theoretically very interesting and may lead to practical consequences as well; however the following features must be taken into consideration before his conception of the diagram is accepted.

1. He experimented upon samples of a very small size.
2. The margins of the ultimate strength values were not very definite.
3. The variations of the ductility might have been caused by secondary influences and do not constitute an unassailable proof.

## APPENDIX 5

### Silumin and Alpac

It is the custom in America to give no particular name to the plain aluminum-silicon alloy with 10% Si or to refer to it as "No 45" (Aluminum Company of America). The modified alloy with

13. Silicon is to the contrary definitely known as Al<sub>3</sub>ax (Alexander Pacz's invention).

In Germany where the 10% Si alloy was used quite a time before Pacz's discovery, it was usually called "silumin," and this name was transferred to the modified alloy. The name "Alpax" was entirely disregarded.

It might prove desirable to retain the name "silumin" for the non-modified alloy in order to define its chemical character, while the name "Alpax" may be most appropriate for the modified product. The author uses these definitions throughout the text.



# PLATES

# PLATE A

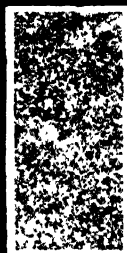
1  
to  
4



5  
to  
8

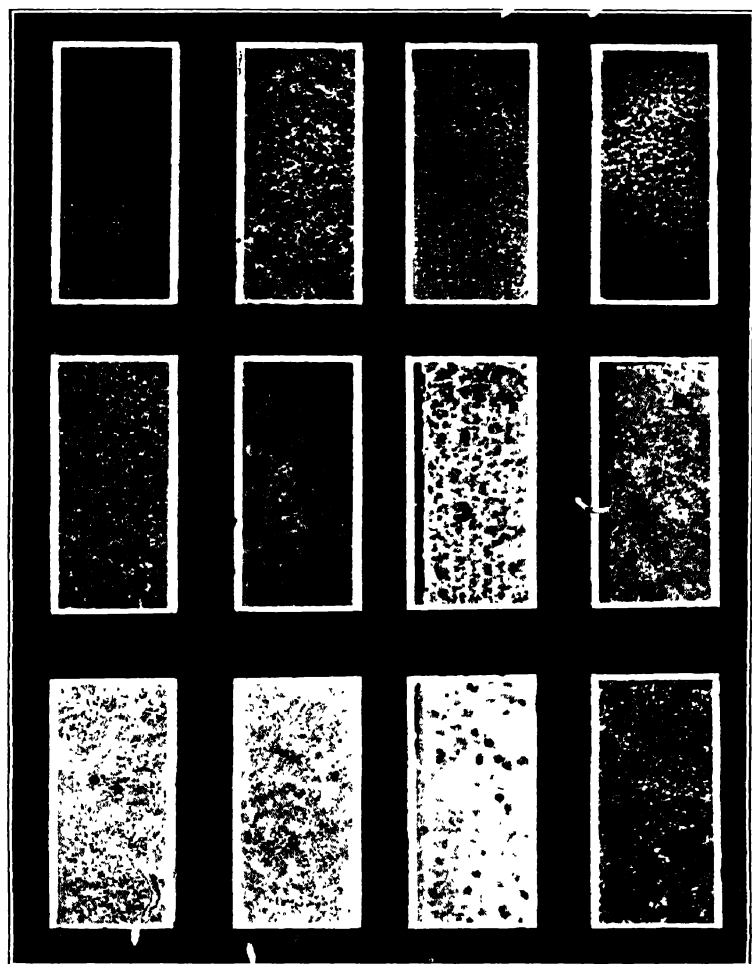


9  
to  
12



Action of 10% Hydrochloric Acid upon aluminum and various aluminum alloys (24 C) for 1 hour

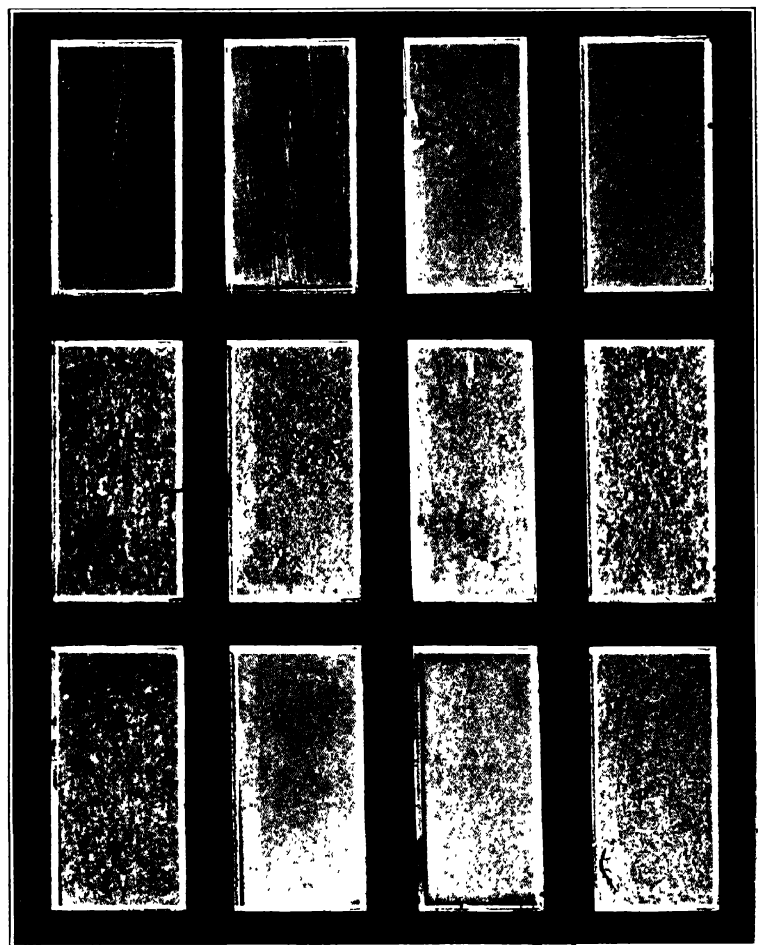
# PLATE B



Action of 10% Hydrochloric Acid upon aluminum and various aluminum alloys (24°C)

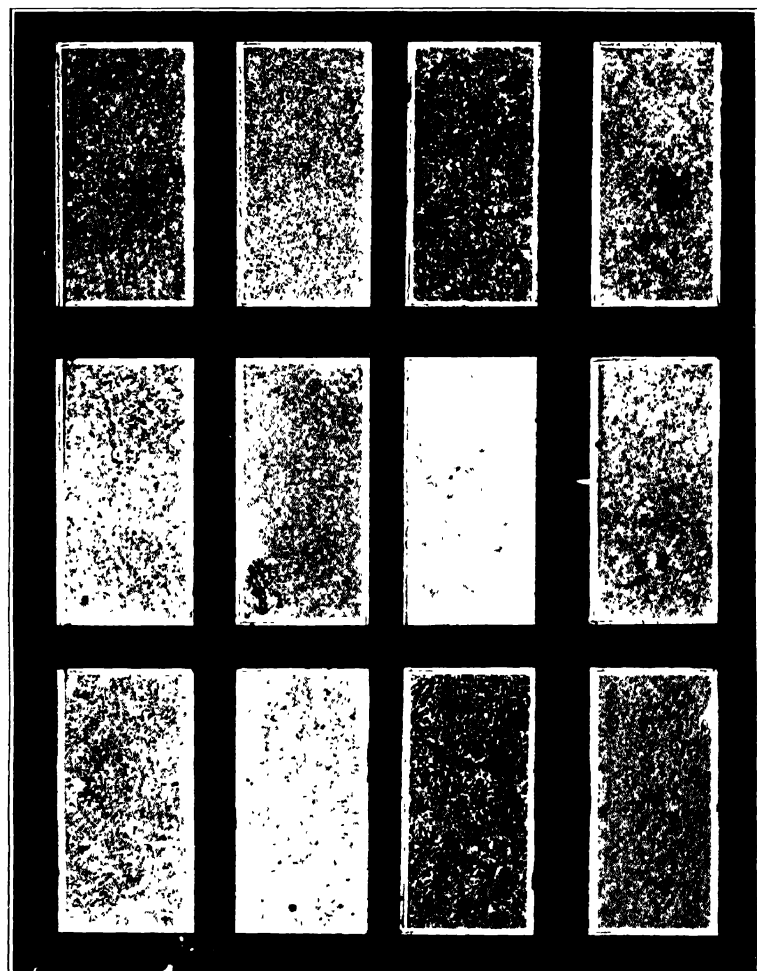


PLATE C



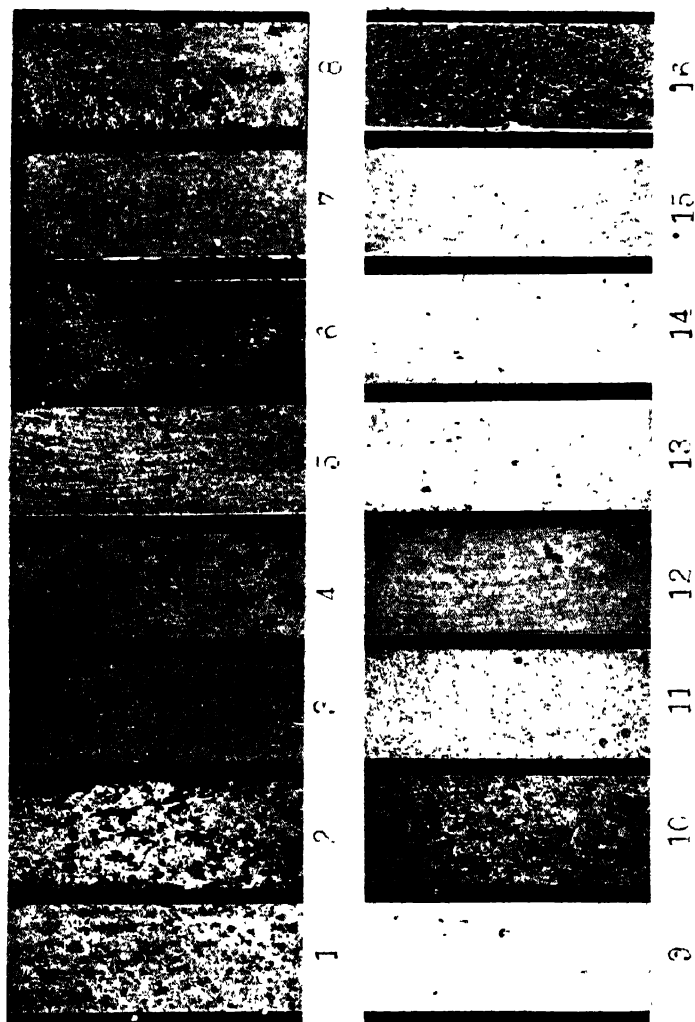
Action of 23% Nitric Acid upon aluminum and its alloy.  
(24 hours, 24° C.)

PLATE D



Action of 23% Nitric Acid upon aluminum and its alloys,  
(24 hours, 24° C ) •

# PLATE E



Action of 50% Acetic Acid at 80°C upon various aluminum alloys (48 hours)

# PLATE 1



Fig. 1 0.2% Fe

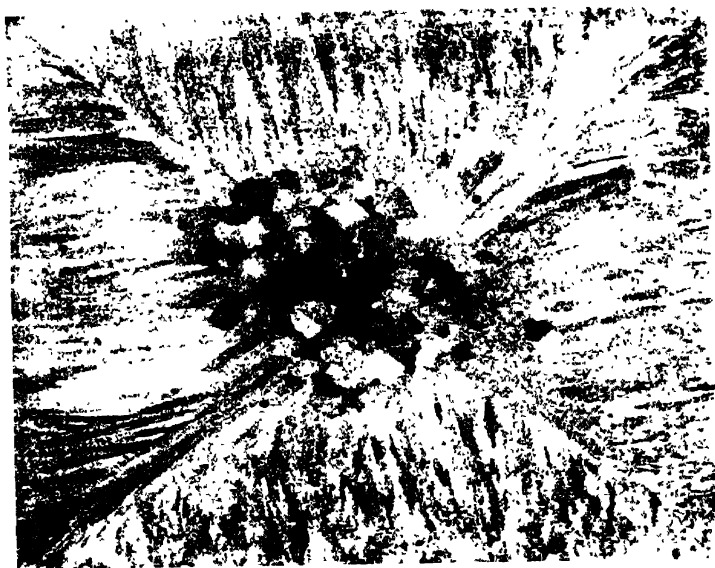


Fig. 2 0.45% Fe  
Macrostructures of aluminum billets

# PLATE 2



Fig. 3. Center of billet  
3" square aluminum billet containing 0.1% Fe. Br hardness at the center 33.4 corner 33.2 X 100

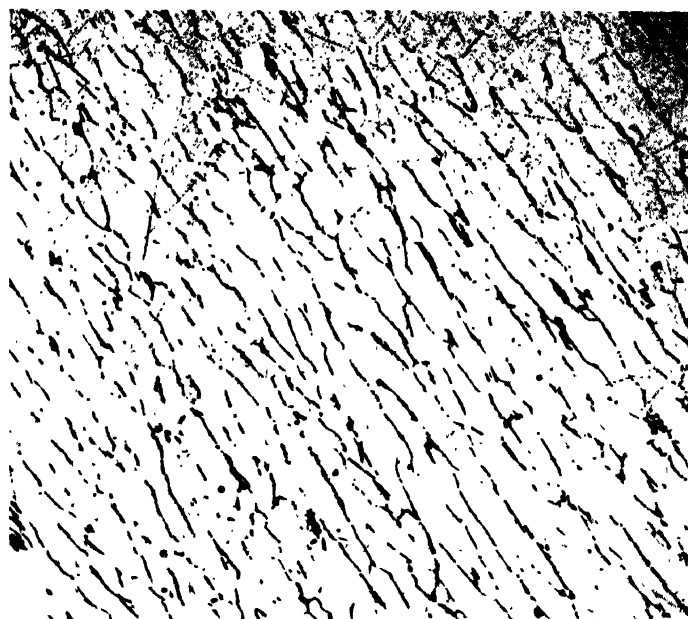


Fig. 4. Corner of billet  
3" square aluminum billet containing 0.1% Fe. Br hardness at the center 33.4 corner 33.2 X 100

PLATE 3



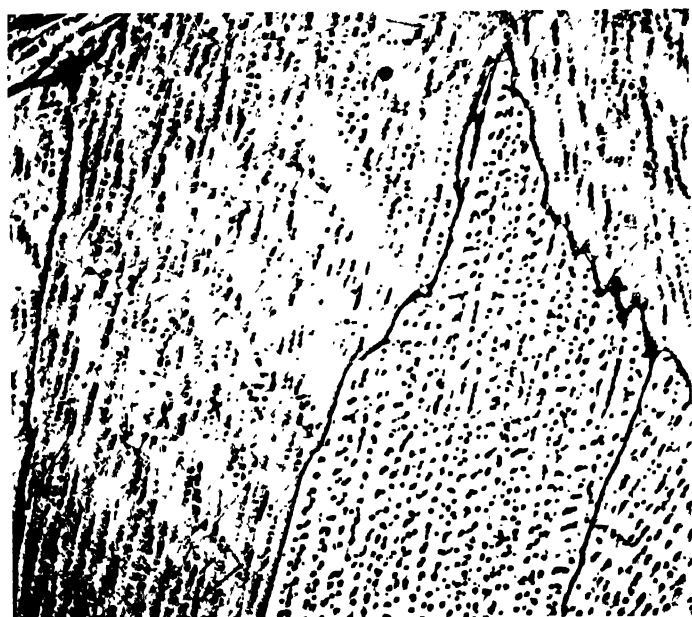
2" round bars of 99.7% aluminum

Fig 5 (top) Chill cast

Fig 6 (bottom) Sand cast

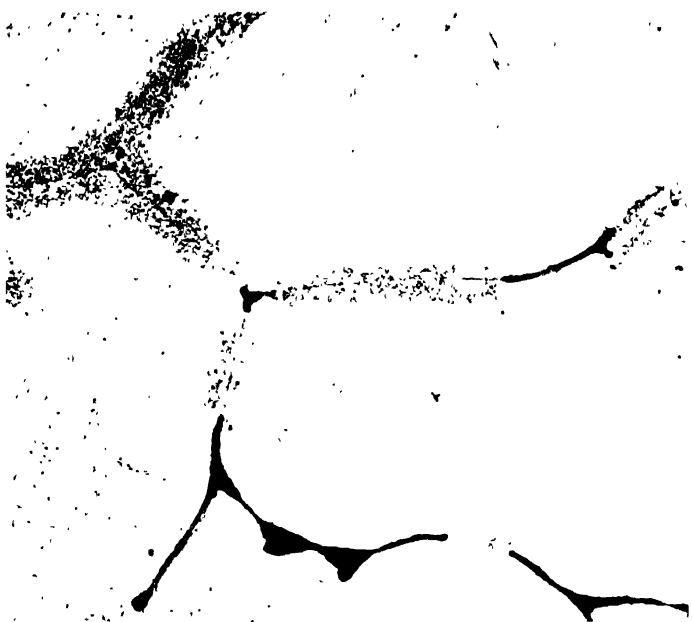
Both X 3.5

# PLATE 4



X 50

Fig. 7. Chill cast



X 250

Fig. 8. Sand cast

1" round bars of purest commercial aluminum, cast at 720°

# PLATE

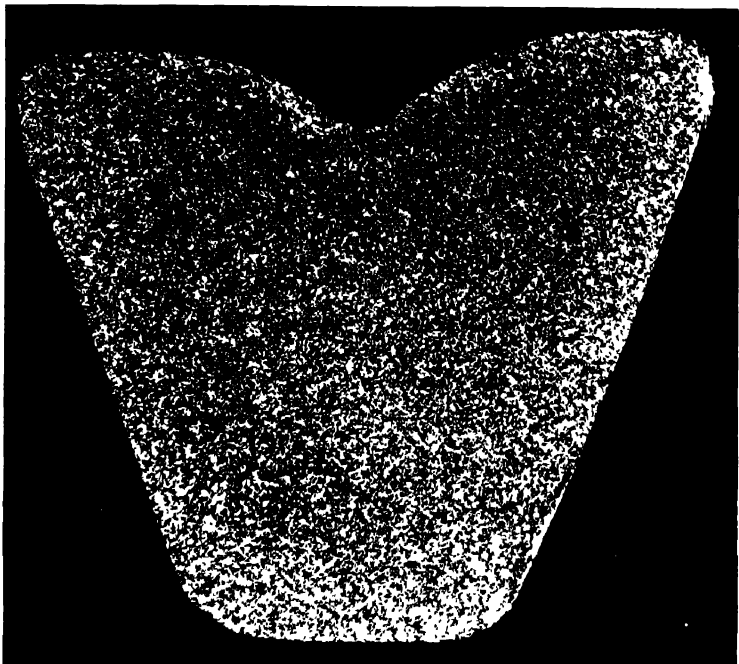


Fig. 9 Cross section of the body

X 2

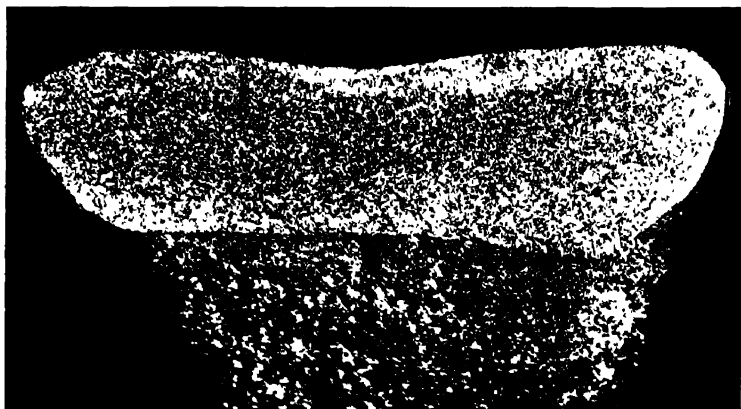


Fig. 10 Cross section of the web  
Notched ingot, small size, 0.75% iron

X 2



# PLATE 6

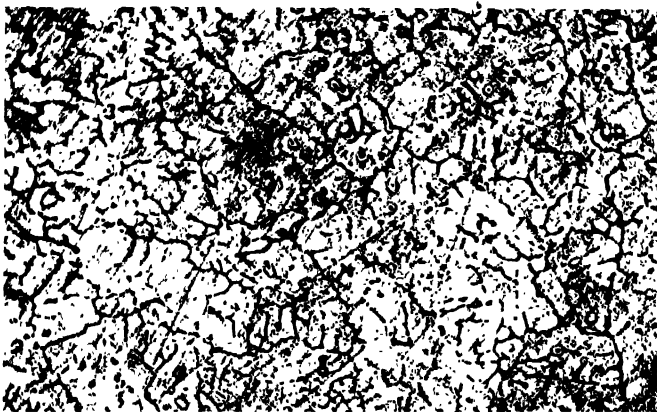


Fig. 11 Bottom of ingot



Fig. 12 Center of ingot  
Commercial 2-d grade aluminum ingot 100 g. Al

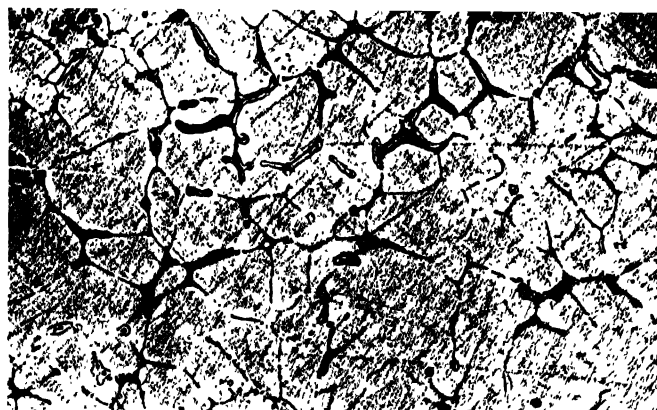


Fig. 13 Top of ingot

All X 100

# PLATE 7

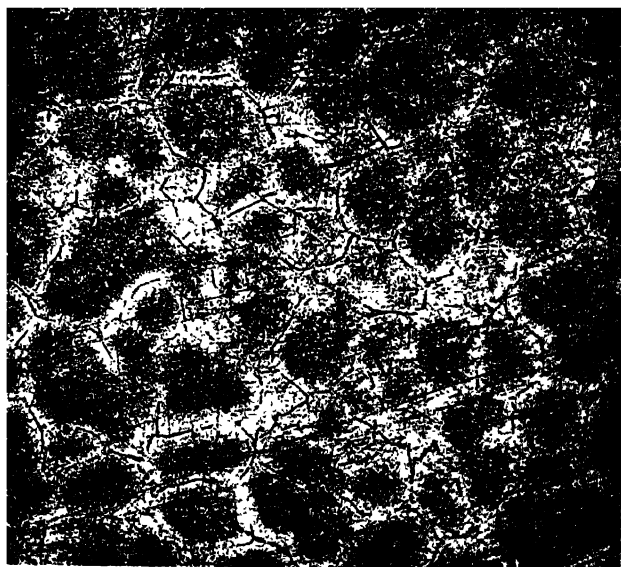


Fig. 14  
Commercial 2-d grade aluminum  
X 100

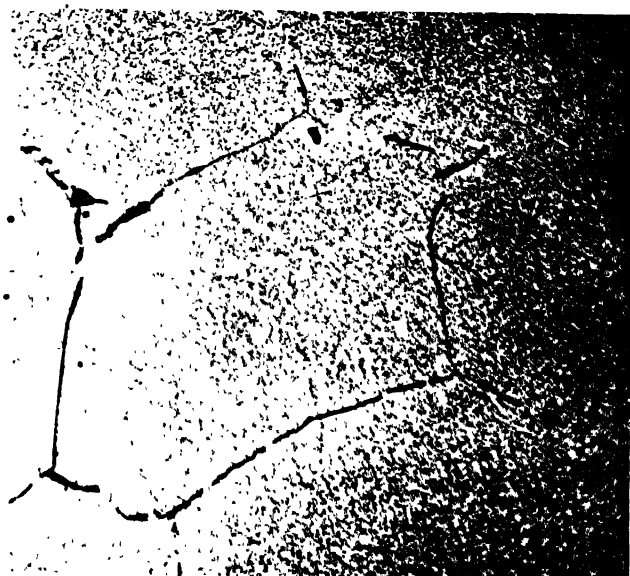


Fig. 15  
1" round bar sand cast 0.75% Fe  
X 500

# PLATE 8



Fig. 16 Hard rolled



Fig. 17 18 h anneal at 450



Fig. 18 18 h anneal at 450

Commercial aluminum sheet (00067) Etched (HCl + HF)

X 100

PLATE 9



Fig. 10 Commercial aluminum sheet, annealed for 2½ h. at 450° X 500

PLATE 10

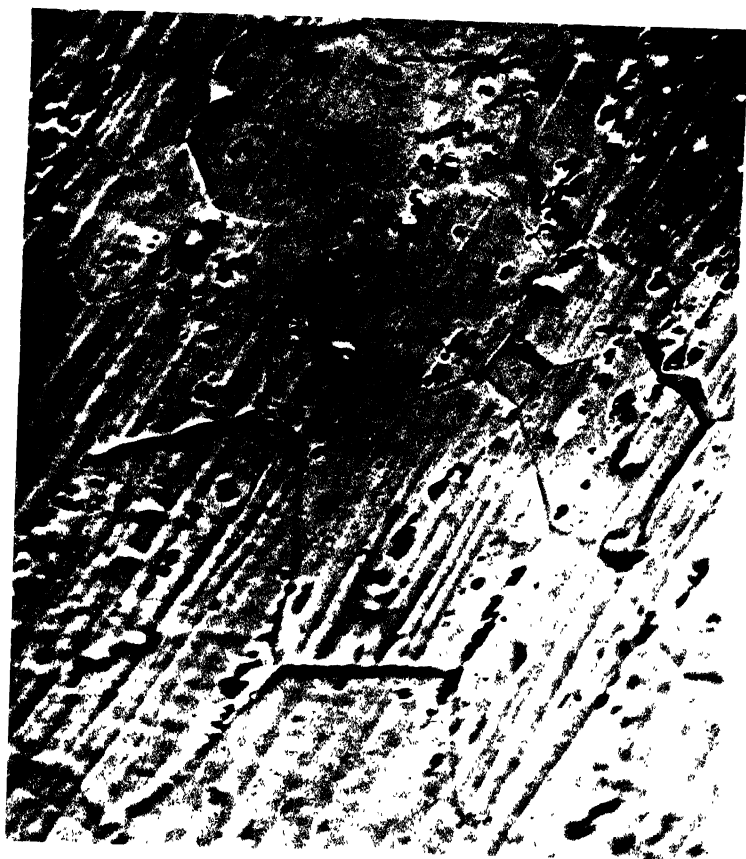


Fig. 20 Commercial aluminum sheet annealed 18 h at 450 X 500

# PLATE 11



Fig. 21. 3 h at 500°C

X 100

Commercial 100%  $Al_2O_3$  aluminum rod annealed at different temperatures

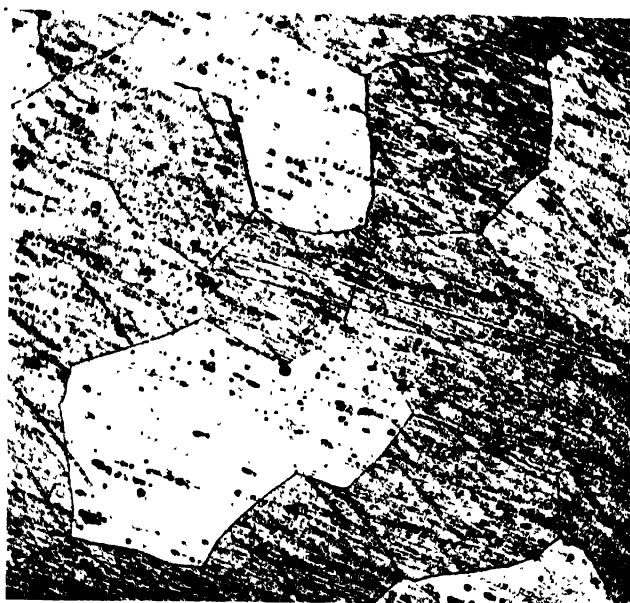


Fig. 22. 3 h at 500°C

X 100

# PLATE 12



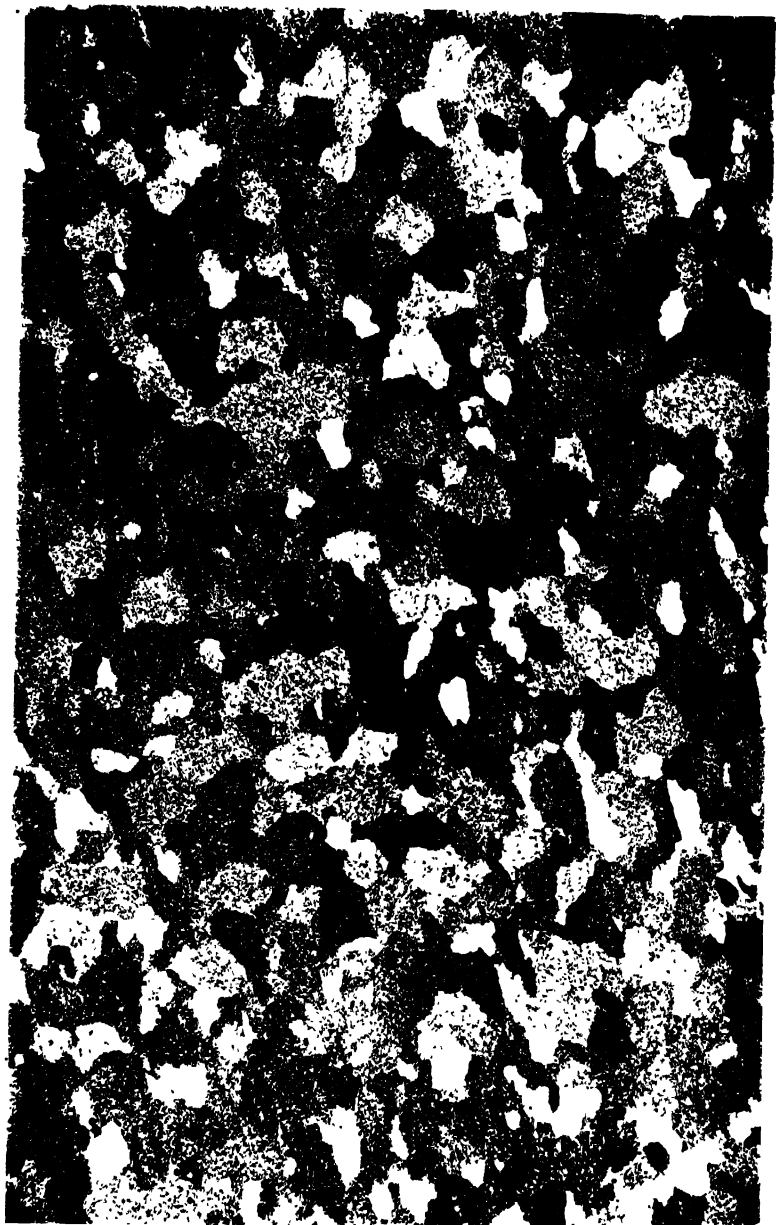
Fig. 23 - 2 hours X 100



Fig. 24 - 12 hours X 100

Purest aluminum sheet  $\frac{1}{8}$ " thick, annealed at 320

PLATE 13



(Courtesy Mr. F. B. Flick.)

Fig. 25 Commercial aluminum sheet, annealed.

X 10



# PLATE 14

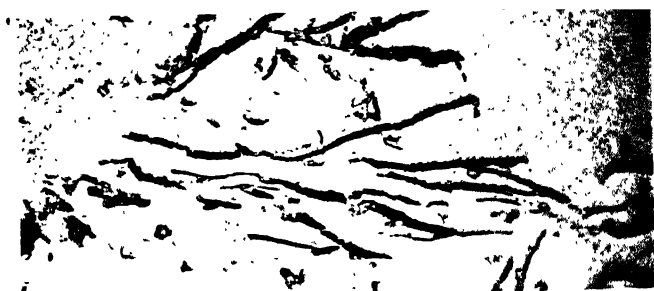


Fig. 29 Sand cast X 500



Fig. 28 Sand cast X 100

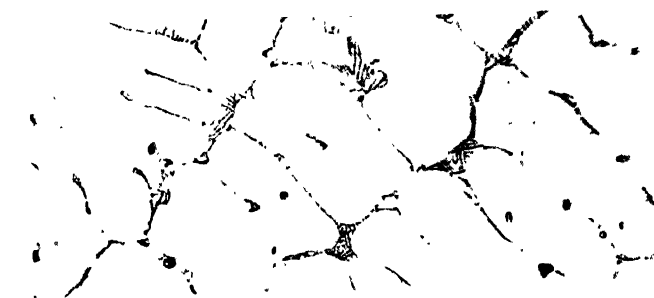


Fig. 27 Chill cast X 500

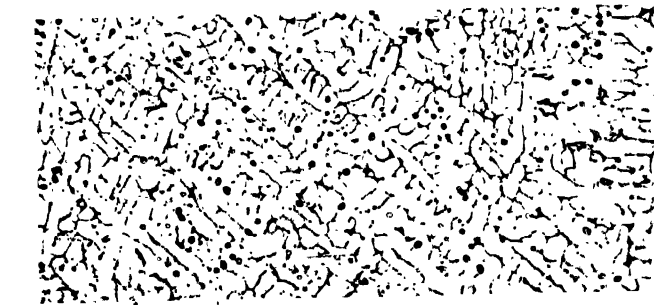


Fig. 26 Chill cast X 100

1" round bar of aluminum containing 0.03% Fe

# PLATE 15



Fig. 37. S and C-t. X 100

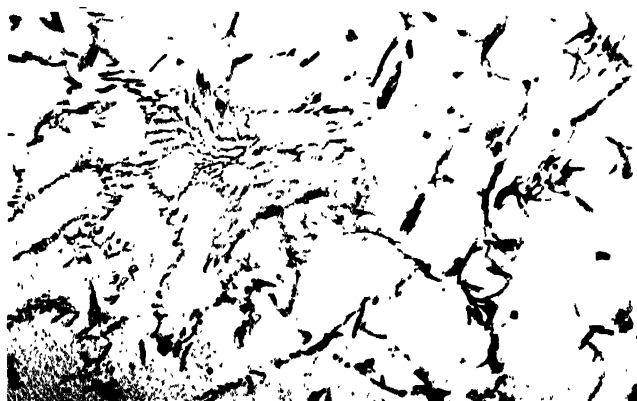


Fig. 38. Chill C-t-t. X 500  
1" round bar of a 2.5% Fe alloy

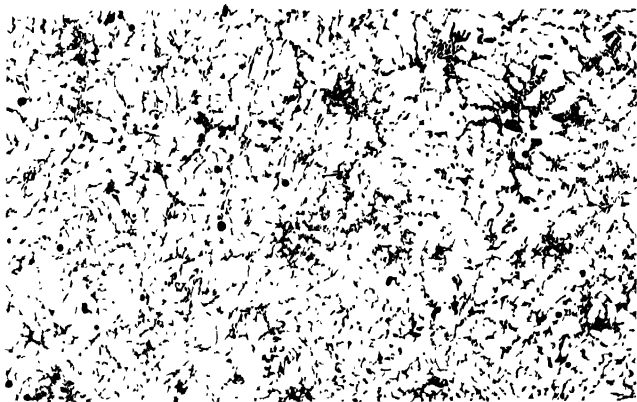


Fig. 39. Chill C-t-t. X 100

PLATE 16

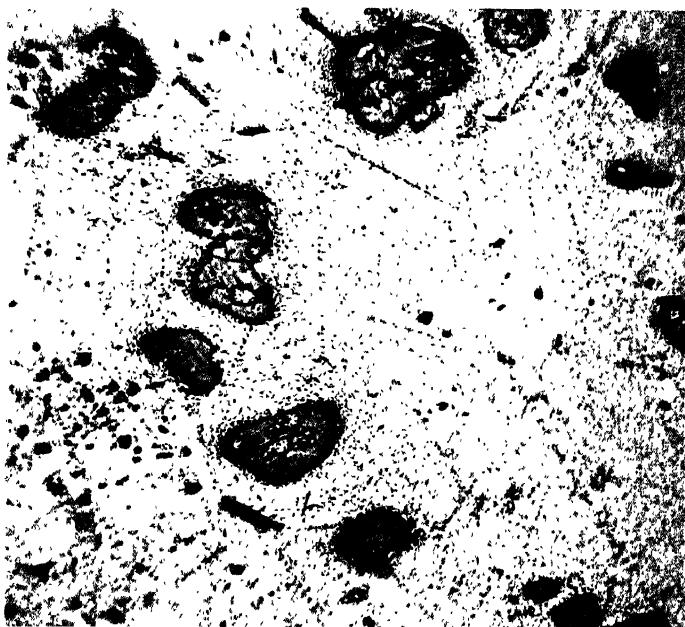


Fig. 33. 2.3% Fe alloy; chill cast, annealed 18 h at 540 °C X 250

PLATE 17



Fig. 34. A primary crystal of FeAl in a 2.3% Fe alloy, sand cast.  
X 500

# PLATE 18



Fig. 35

X 100  
4.4% Fe alloy chill cast



Fig. 36

X 500

# PLATE 19

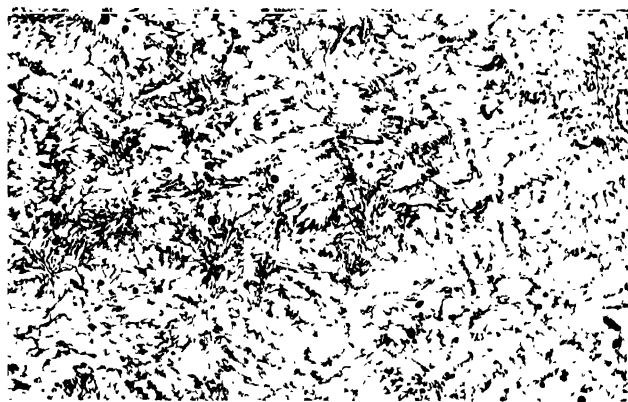


Fig. 37 Chill cast X 103



Fig. 38 Chill cast X 500  
1" round bars of 1.5% Fe, 2.5% Si alloy



Fig. 39 Sand cast X 100

PLATE 20

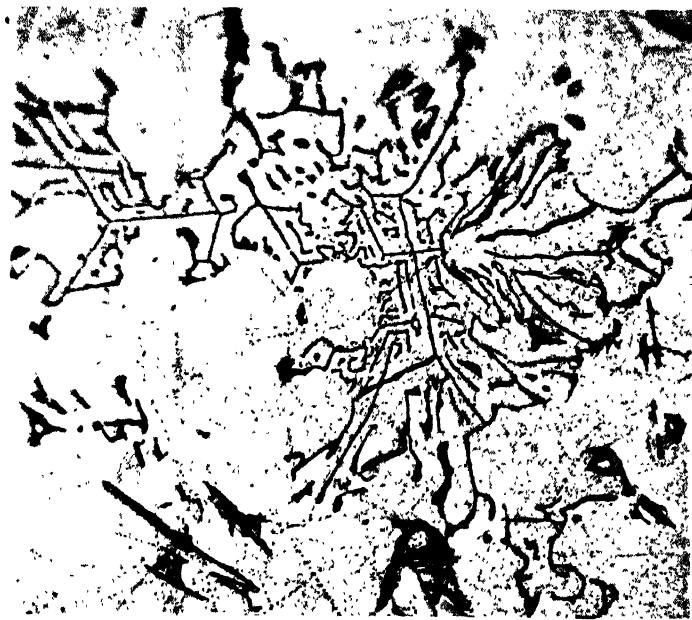


Fig. 41 "Chinese script" sand cast



Fig. 40 Average structure of 1" round bar of 15% Fe + 20% Si alloy sand cast

# PLATE 21

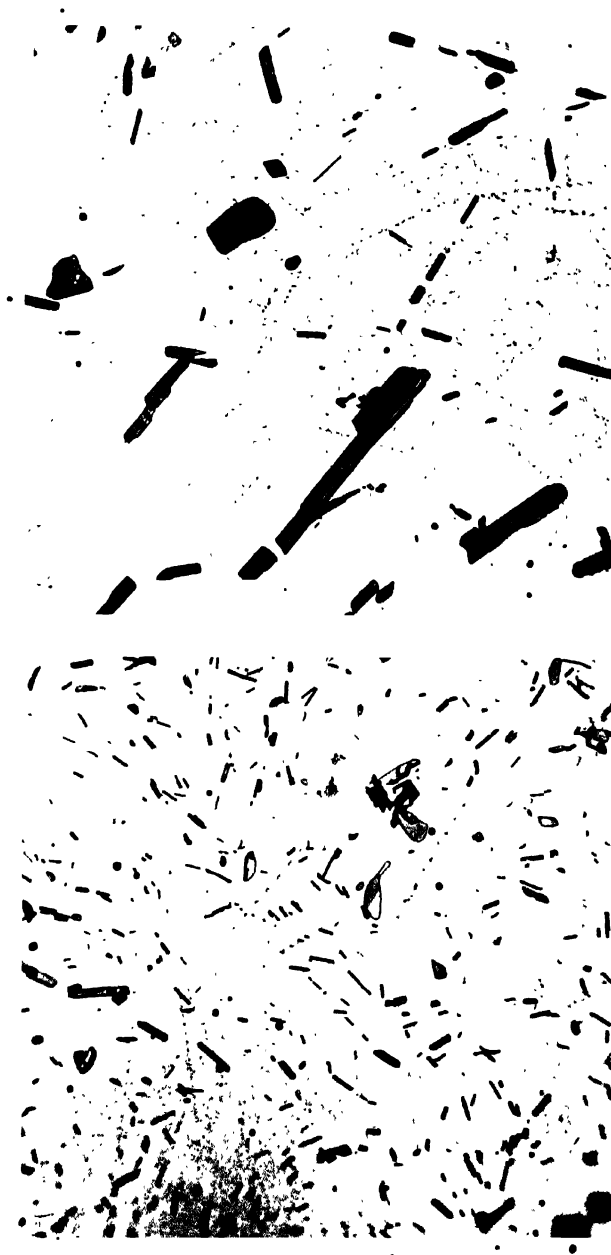


Fig. 42 Chill cast

X 250

Al-Fe-Si alloy (1.5% Fe, 2.0% Si) cast and quenched after 12 h at 530

Fig. 43 Sand cast

X 200



# PLATE 22

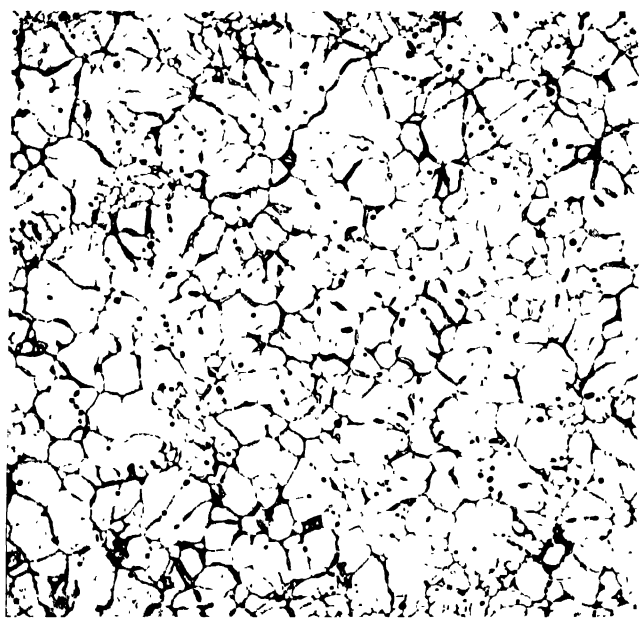


Fig. 44  
1" square bar of 1.65% Mn Fe alloy chill cast at 700°C  
X 100

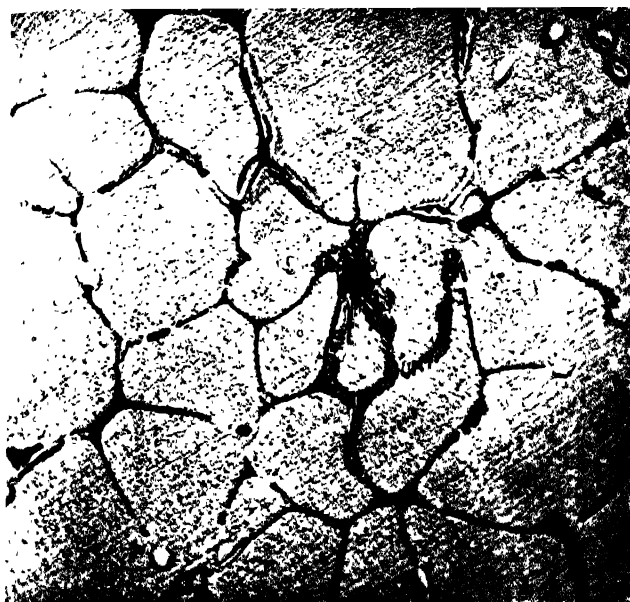
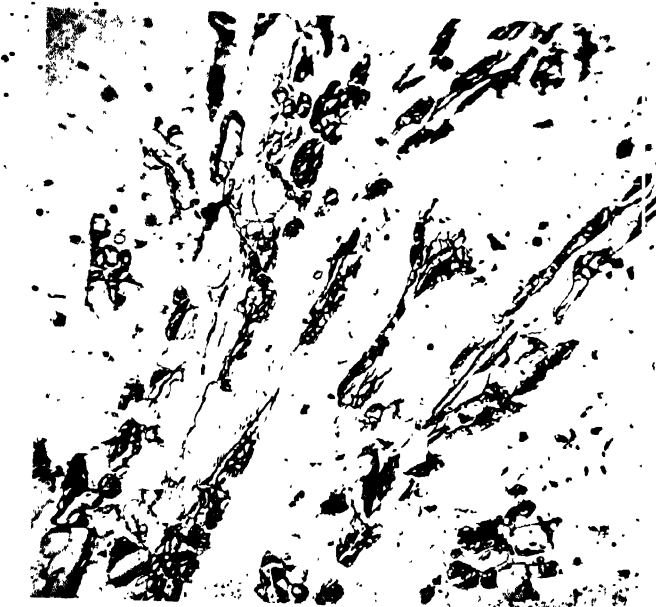


Fig. 45  
1" square bar of 1.65% Mn Fe alloy chill cast at 700°C  
X 500

PLATE 23



X 500

Fig. 4- 5% Mn sand cast



X 500

Fig. 4- 2% Mn sand cast  
1" round bars of Al-Mn alloys (0.2% Fe) as cast

PLATE 24

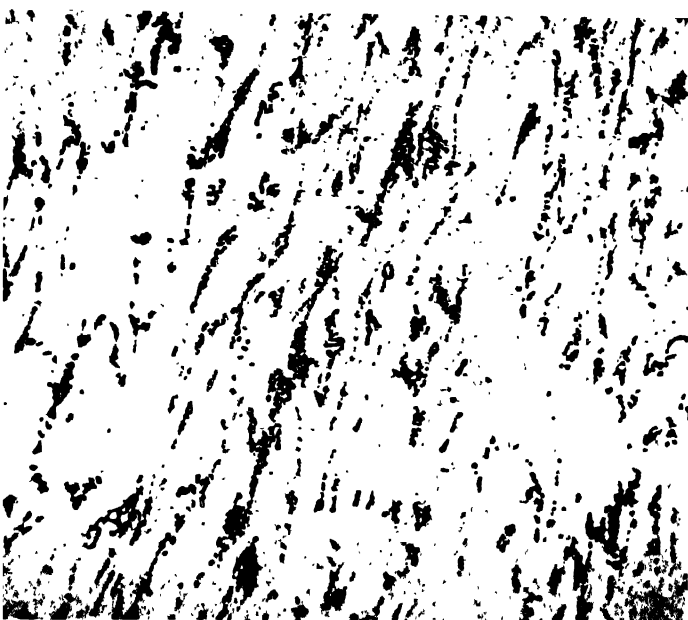


Fig. 48. Slightly etched  
1% square bar of 1.05% Mn - 0.06% Fe, forged at 500 to 550° h at 500°

X 250

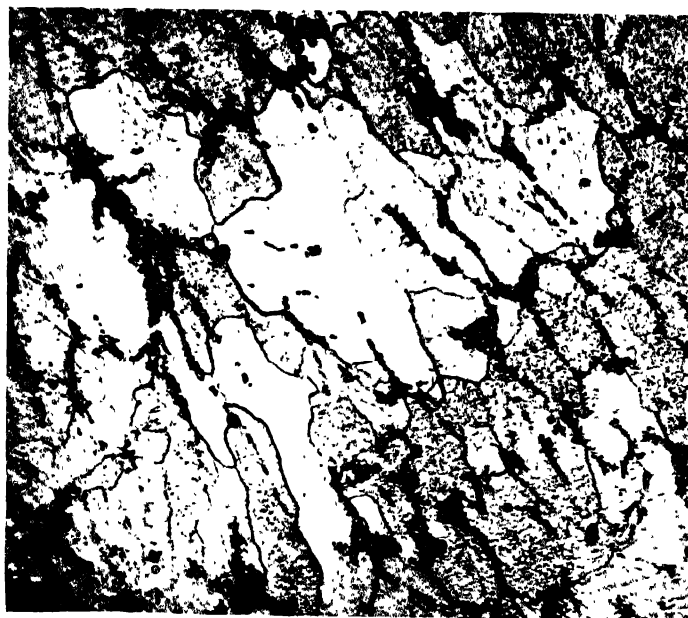
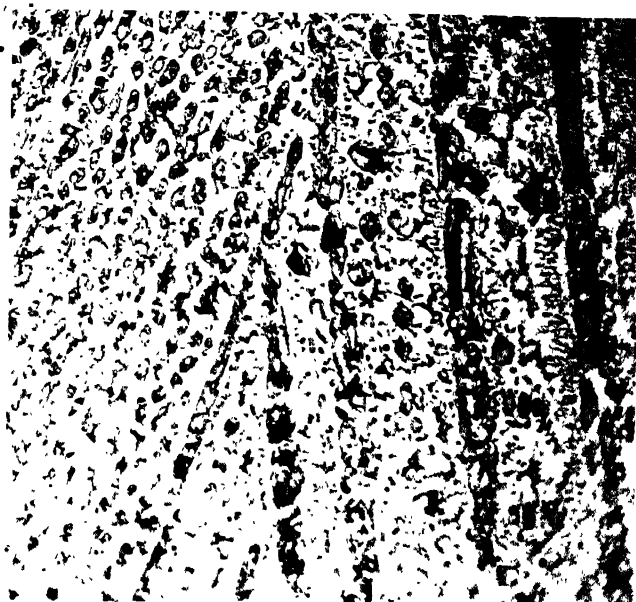


Fig. 49. Repolished, deep etched  
1% square, annealed 7 h at 500°

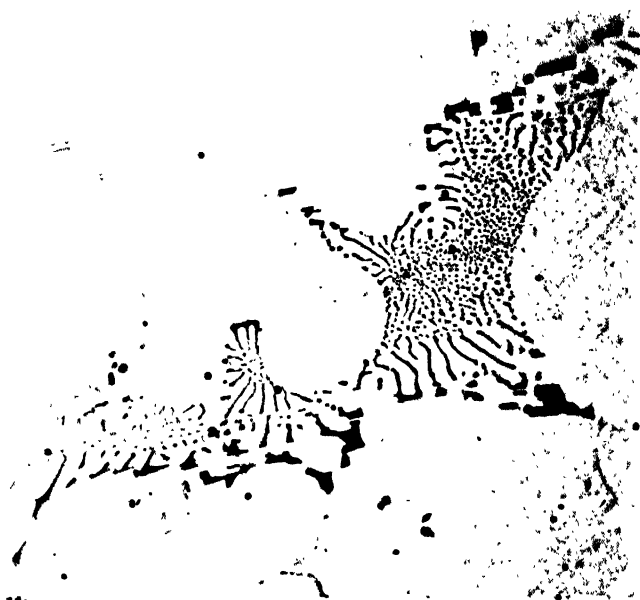
X 250

# PLATE 25



X 500

Fig 31 14% Ni chill cast



X 500

Fig 30 0.7% Ni sand cast

Low and high aluminum-nickel alloys as cast

# PLATE 26

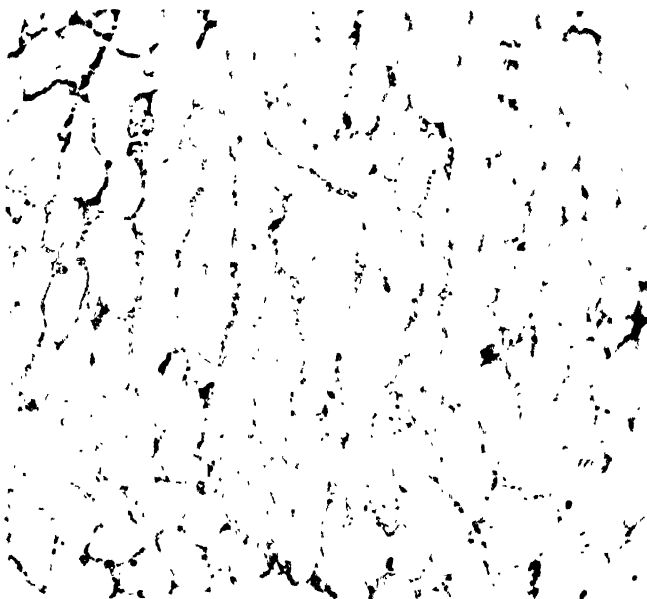


Fig 52. 15% Ni + 0.5% Fe (1" round bar) X 500

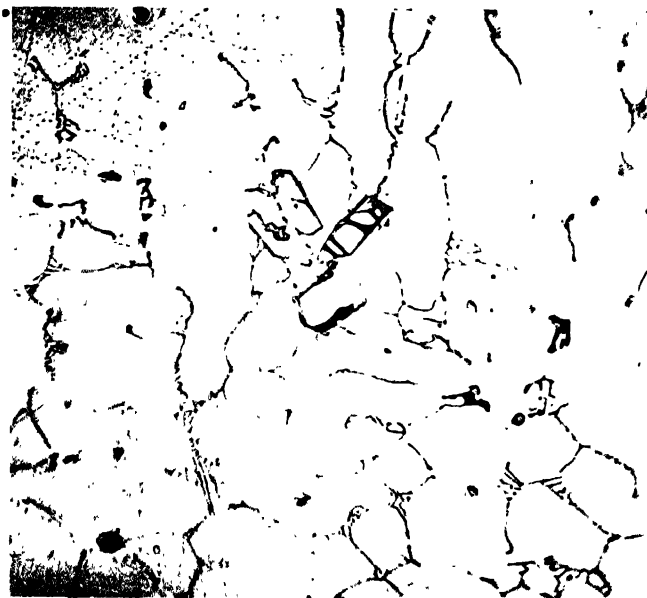


Fig 53. 15% (Cr + 0.5% Fe (1" plate) X 500

(Chill cast alloys of commercial aluminum with Ni and Cr)

PLATE 27

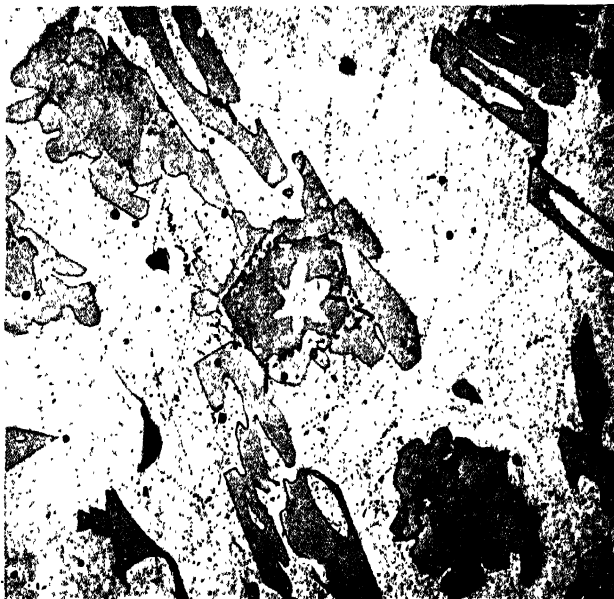


Fig. 54 Al-Mn-Fe alloy  
Sand cast alloy bars, containing 2.5% Fe and 2-2.5% Mn or Ni respectively X 250

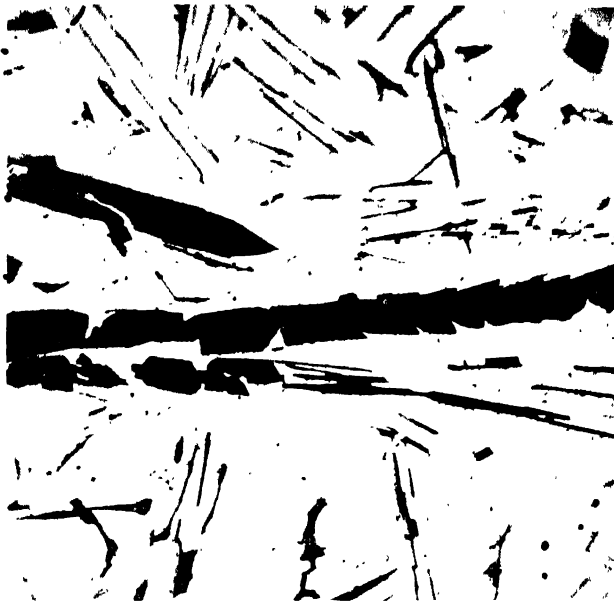


Fig. 55 Al-Ni-Fe alloy  
Fe and 2-2.5% Mn or Ni respectively X 250

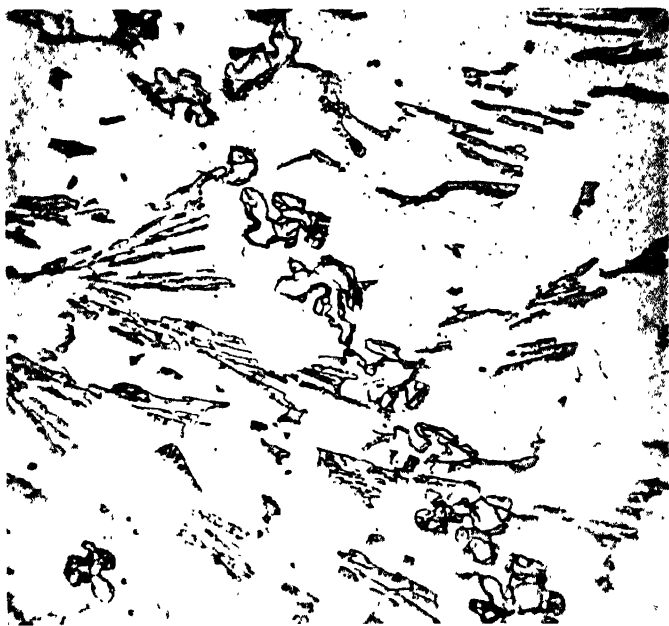


Fig. 56. 2% Fe, 2% Ni, 2% Mn

X 250

Sand cast alloys containing iron, nickel, and manganese

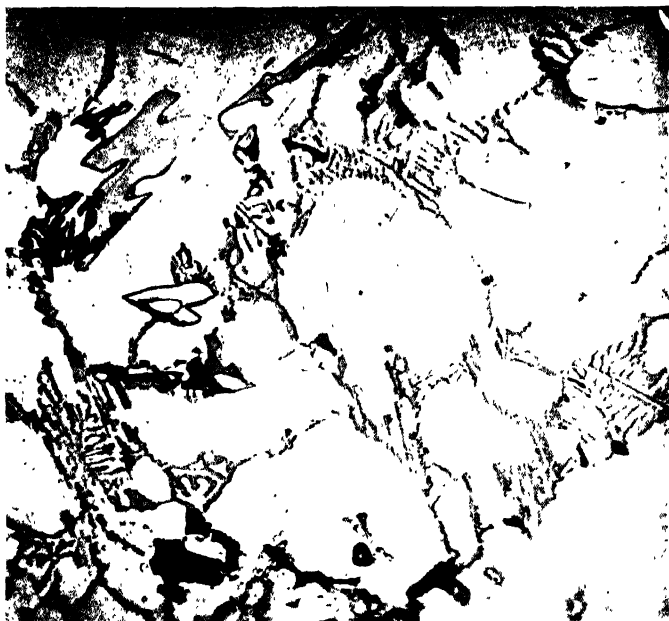


Fig. 57. Same plus 4% Cu

X 250

with or without copper

PLATE 29



Fig. 48. Non-modified  
1" square bars of 10 5/8% Si alloy (Fe = 0.2%), sand cast at 0.50"

X 100

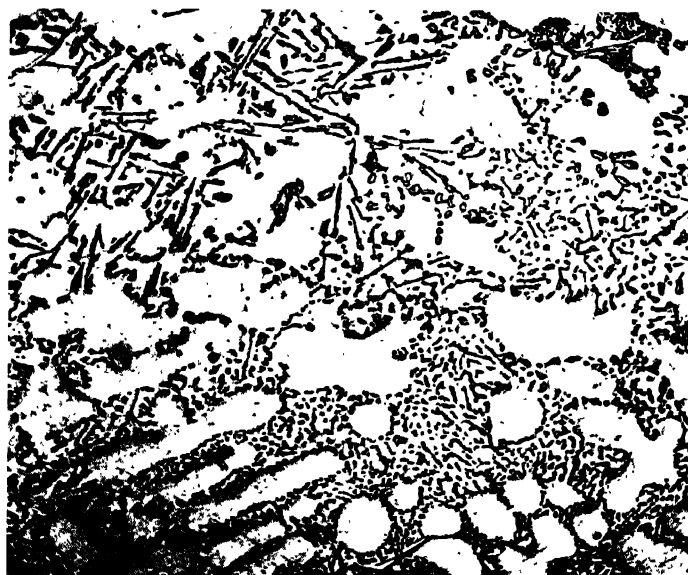


Fig. 49. Sodium treated  
1" square bars of 10 5/8% Si alloy (Fe = 0.2%), sand cast at 0.50"

X 100



# PLATE 30

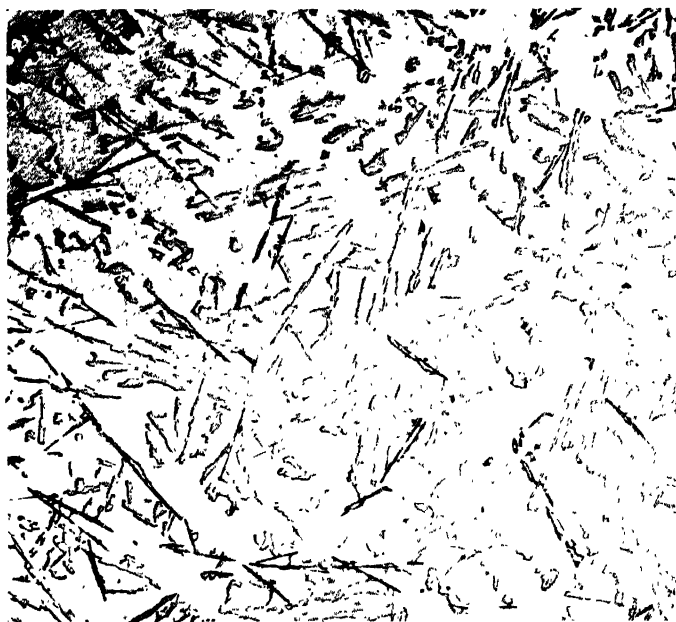


Fig 60 Non-modified (Silumin) X 100  
 1" square bars containing 10.5% Si and 0.45% Fe, sand cast

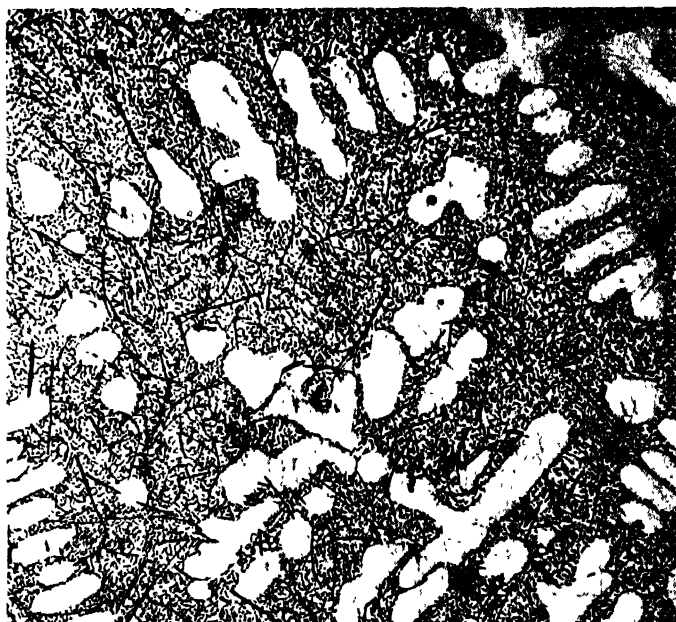


Fig 61 Sodium treated (Alpa) X 100  
 1" square bars containing 10.5% Si and 0.45% Fe, sand cast

PLATE 31

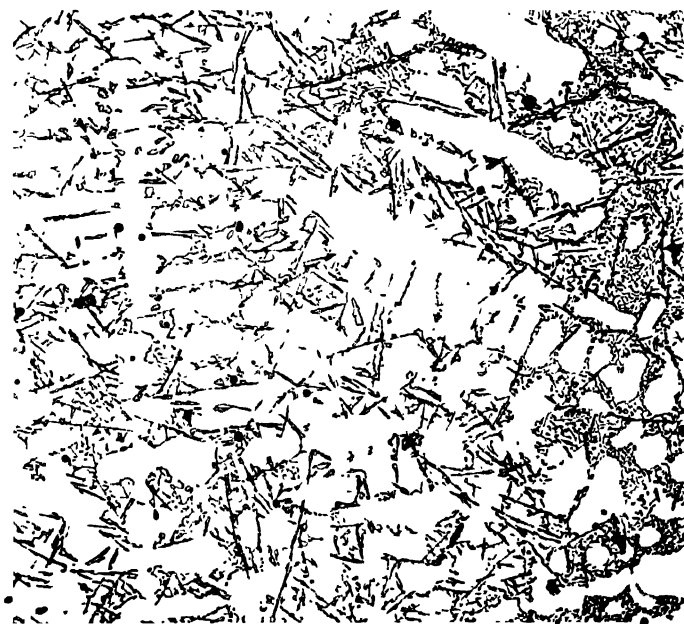


Fig 62 105% Fe, fair casting

X 100



Fig 63 105% Fe, bad casting

X 100

Commercial slumilumin castings produced under poor foundry conditions

# PLATE 32



Fig. 64 A moderately good casting  
Silumin alloy (5% Sn, 80% Fe) X 250



Fig. 65 A bad casting  
Silumin alloy (5% Sn, 80% Fe) X 250

PLATE 33 (See page 253)

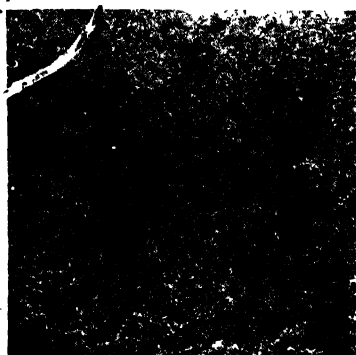


Fig. 66

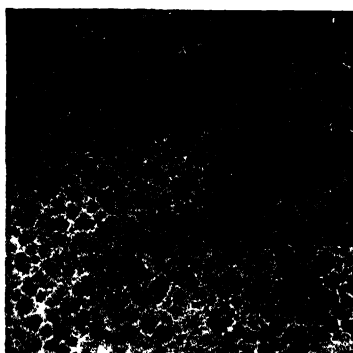


Fig. 67

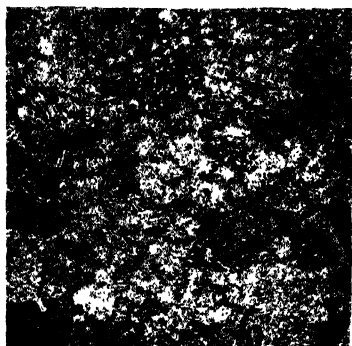


Fig. 68

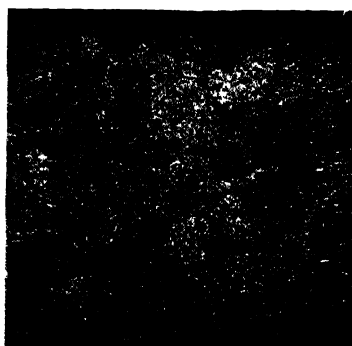


Fig. 69



Fig. 70a



Fig. 70c



Fig. 70b

PLATE 34

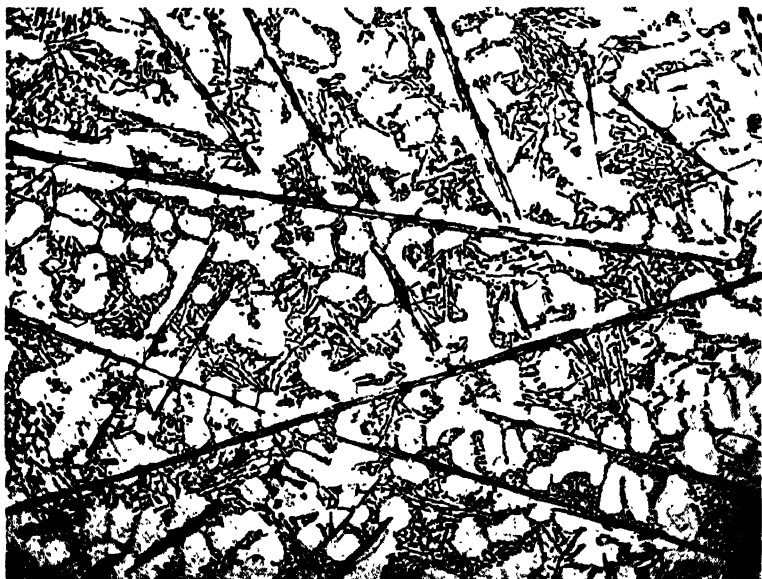


Fig. 71 (Bottom) good metal (1.1% Fe) vacuum remelted Both X 80  
 Fig. 72 (Top) bad metal (1.7% Fe) remelted

PLATE 35



Fig. 73. A bad aluminum casting (with 1.05% Fe) remelted and sodium treated

X 100

PLATE 36

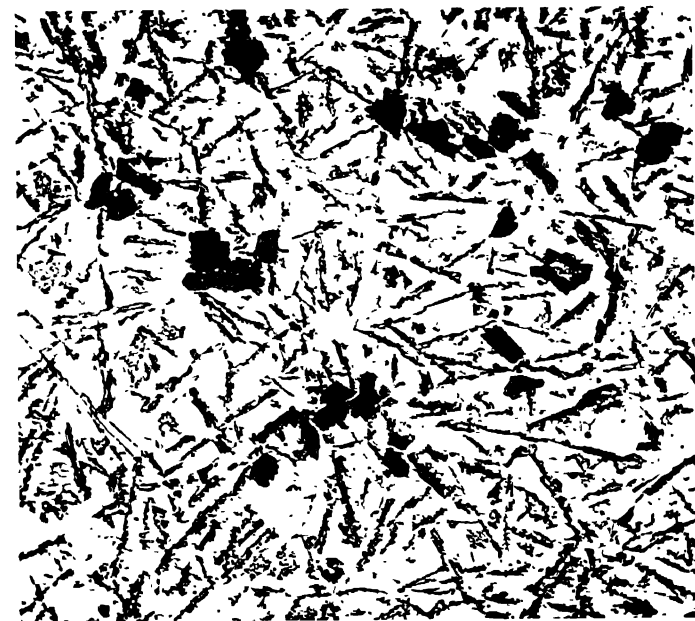


Fig. 74. Non-modified (Aluminum) X 100  
" 1" round bar of 12.5% Si and approx. 0.6% Fe sand cast at 670°C.



Fig. 75. Sodium treated (Aluminum) X 100  
" 1" round bar of 12.5% Si and approx. 0.6% Fe sand cast at 670°C.

PLATE 37

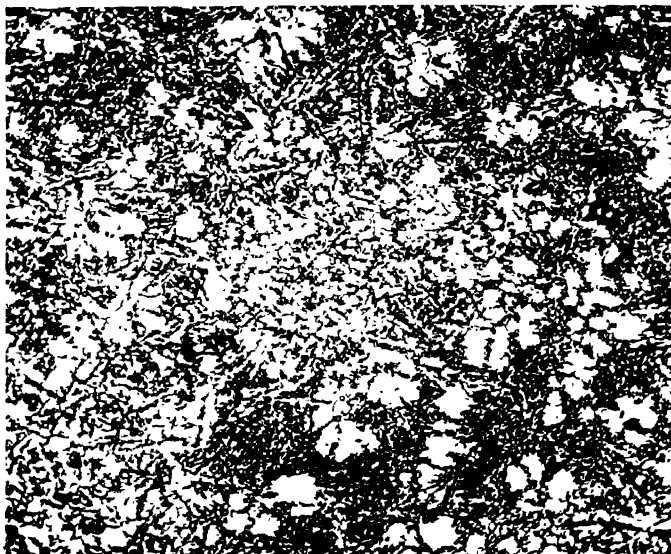


Fig. 76. Non-modified  
1" round bars of 12.5% Si alloy  
chill cast at 650° X 100

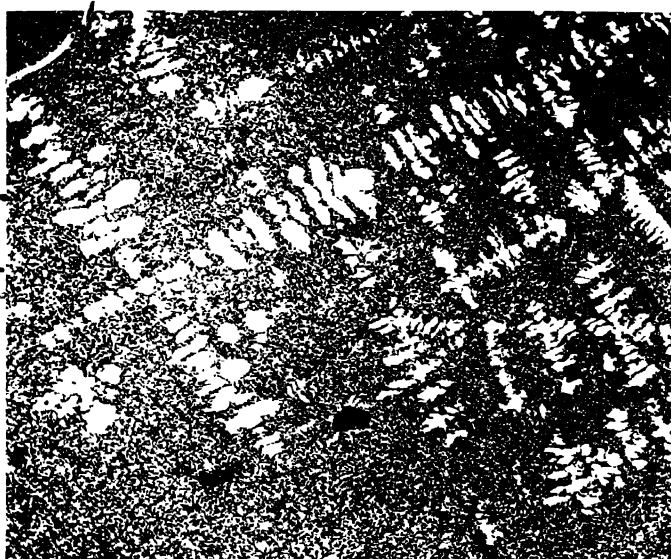


Fig. 77. Sodium treated  
1" round bars of 12.5% FeO alloy  
chill cast at 650° X 100



PLATE 38

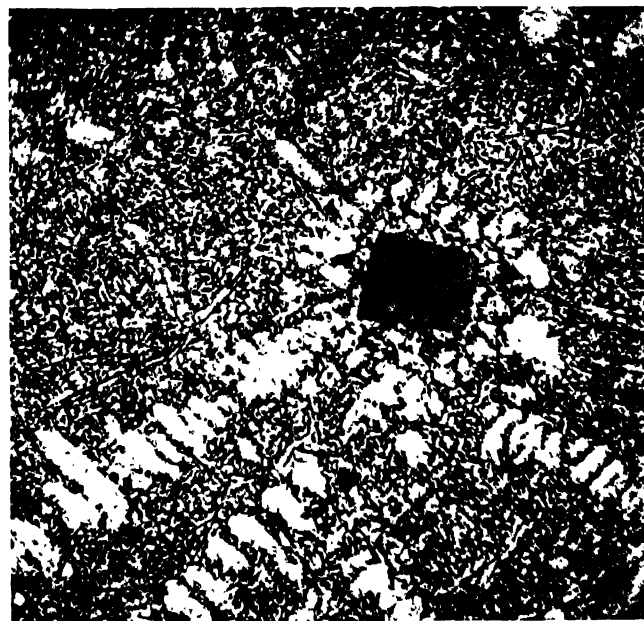


Fig. 78. Chill cast  
1" round bars of "alpa" (12.5% Si - 0.6% Fe) sodium treated

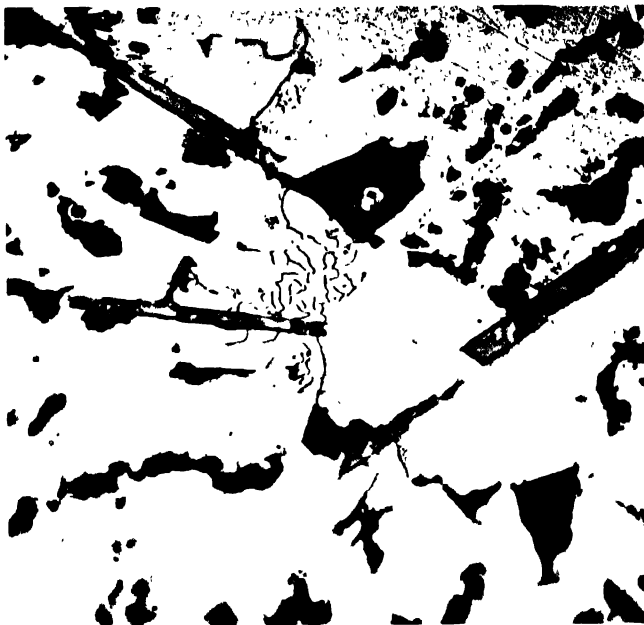


Fig. 79. Sand cast  
1" round bars of "alpa" (12.5% Si - 0.6% Fe) sodium treated



Fig 80

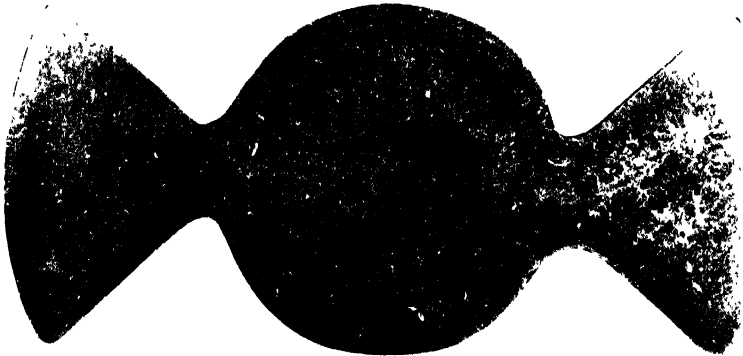


Fig 81

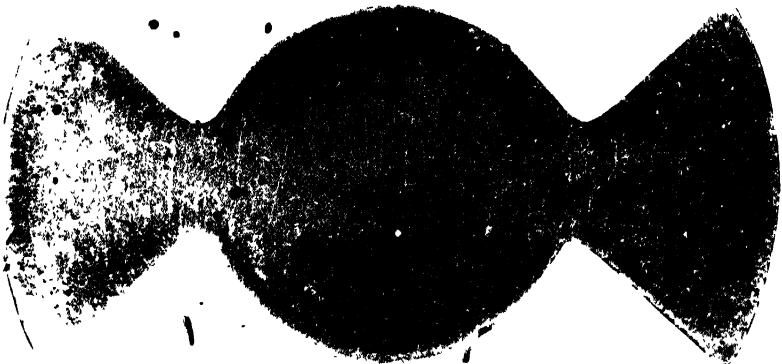


Fig 82

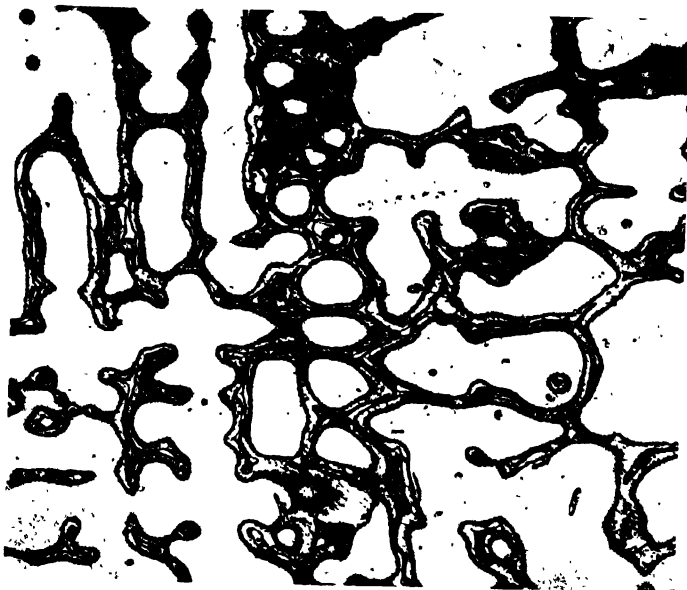


Fig 83 As cast  
1" round bar of a 3% Cu alloy (0.2% Fe) sand cast at 720°C  
X 100



Fig 84 20 h 500°C ann-d  
1" round bar of a 3% Cu alloy (0.2% Fe) sand cast at 720°C  
X 100

# PLATE 41

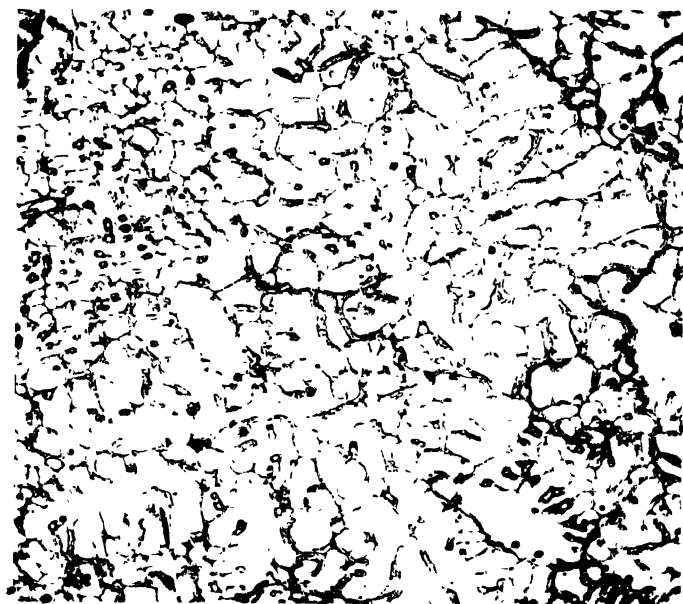
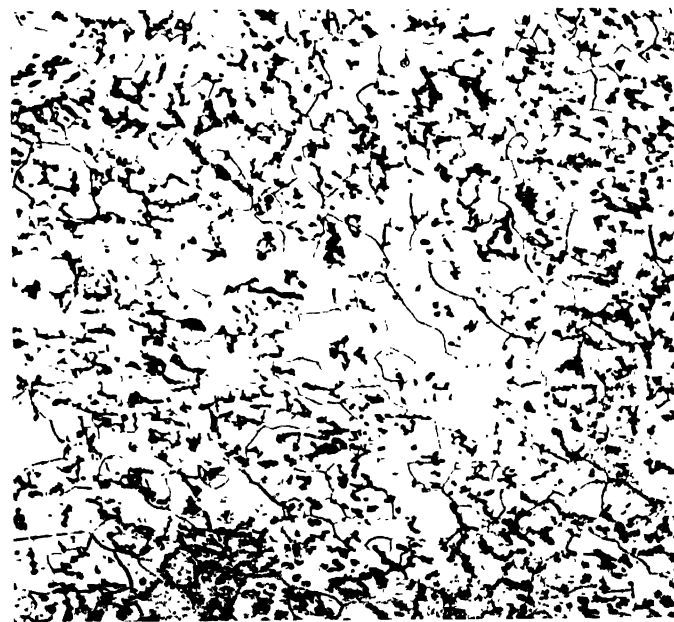


Fig. 85  
X 100



Fig. 86  
X 500



X 100

FIG. 87. A bar of 3% Cu - 0.8% alloy, forged at 450°C from 1" to 1/2" square, annealed 7 h at 500°C, quenched



X 500

FIG. 88

# PLATE 43



Fig 80 As-sand cast  
5% Cu alloy X 250

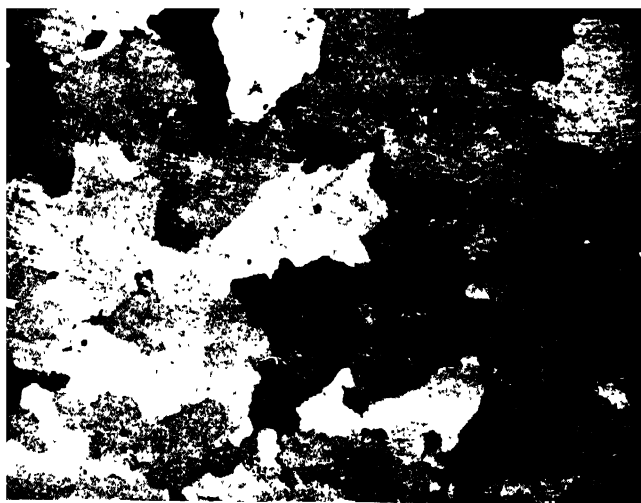


Fig 00 10 h at 450°C w q-d  
square sand cast bar X 8

# PLATE 44

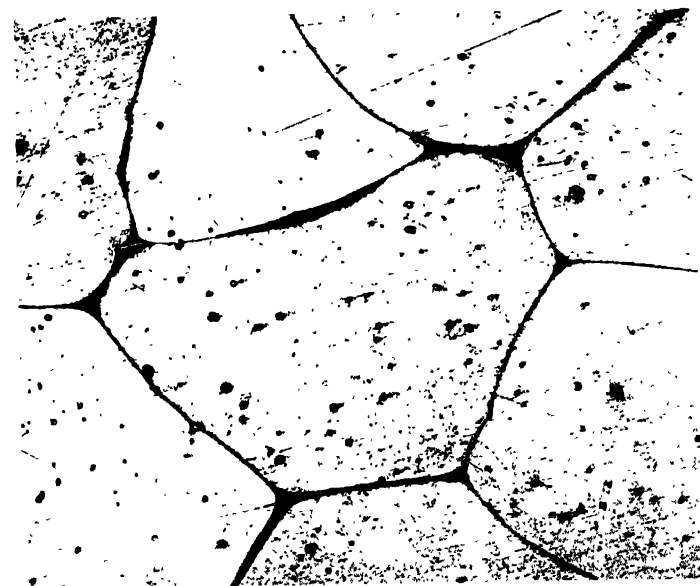


Fig 01 Sand cast, quenched at 520 W 9-10 Cu alloy as sand cast and as forged at 480°C X 100

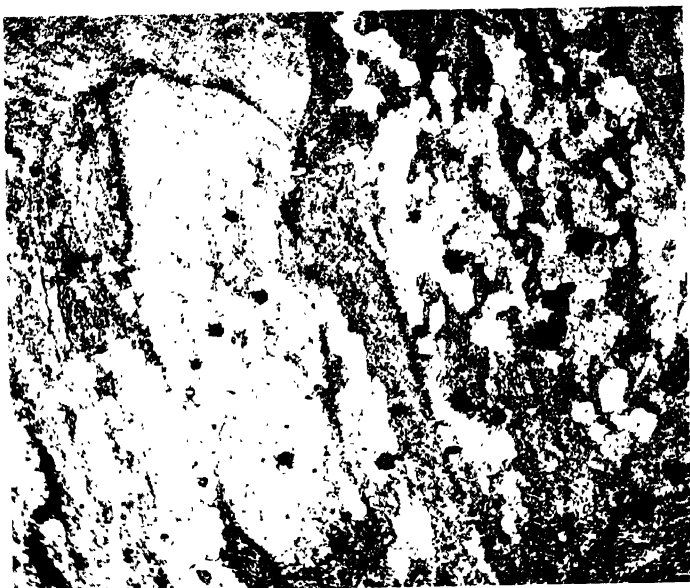


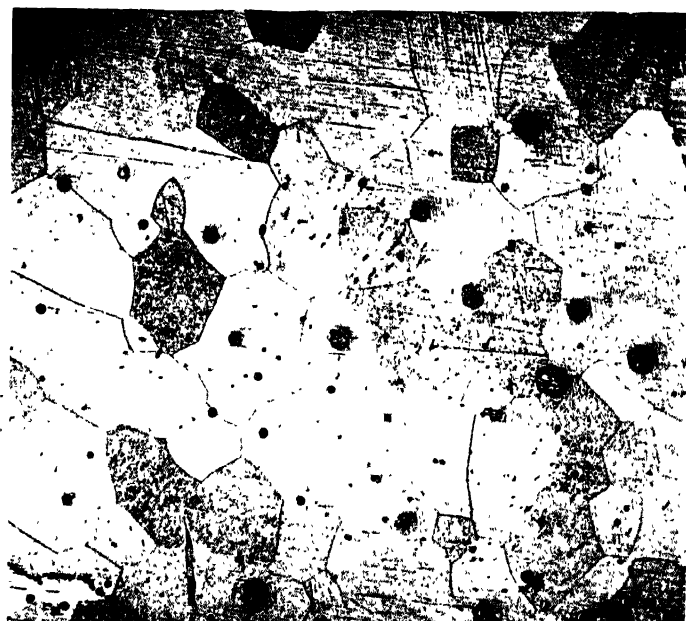
Fig 02 Forged 75% air cooled X 100

# PLATE 45



X 100

Fig. 01 5 h 480° air cooled  
forged and heat treated



X 100

Fig. 03 5 h at 500° w q-d  
5% Cu 10.2% Fe alloy



PLATE 46

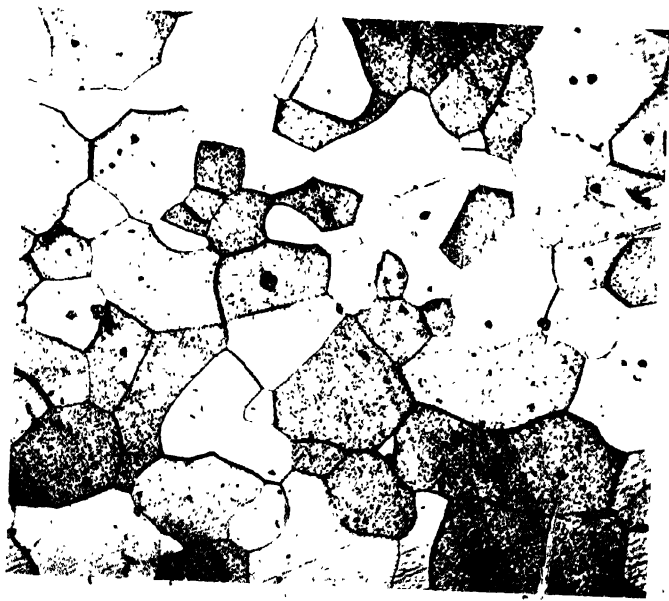


Fig 05  
5% Cu alloy forged 75%, heat treated (8 h 520°, w 9-d, 18 h, 125°)  
X 100



Fig 06  
5% Cu alloy forged 75%, heat treated (8 h 520°, w 9-d, 18 h, 125°)  
X 500

PLATE 47

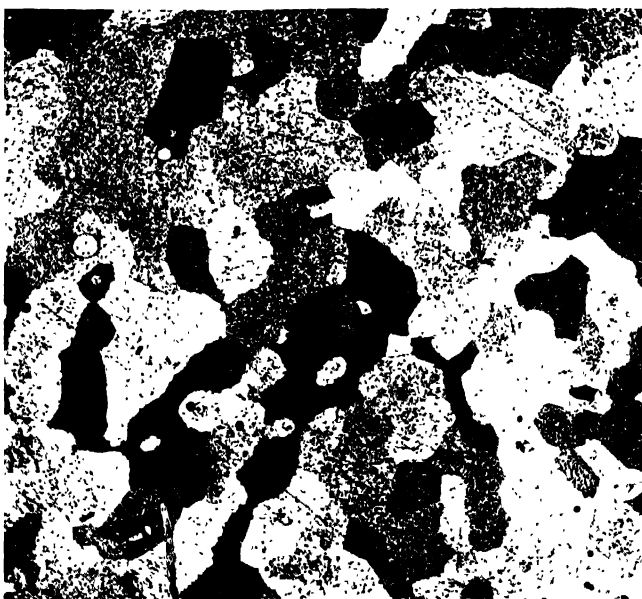


Fig 07  
5% Cu alloy forged 75%, heat treated 8 h at 480°, w. q-d, 3 h at 180°  
X 100

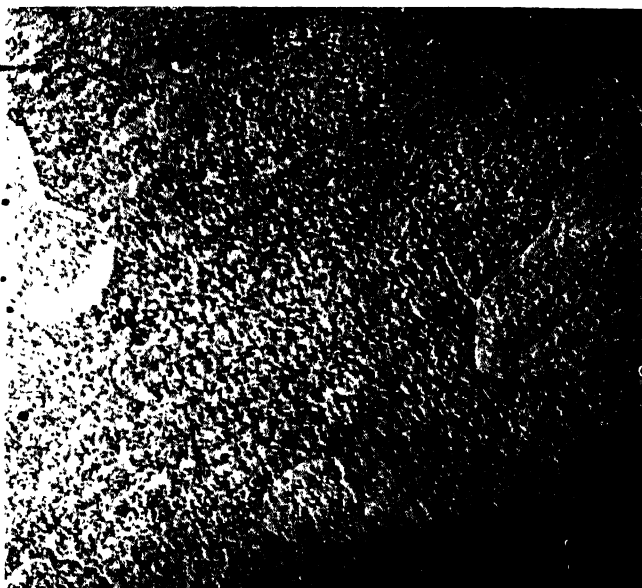
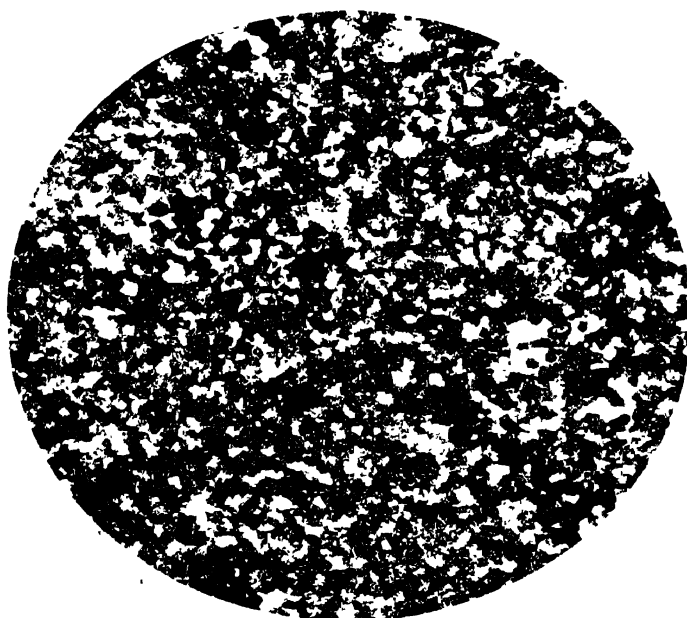


Fig 08

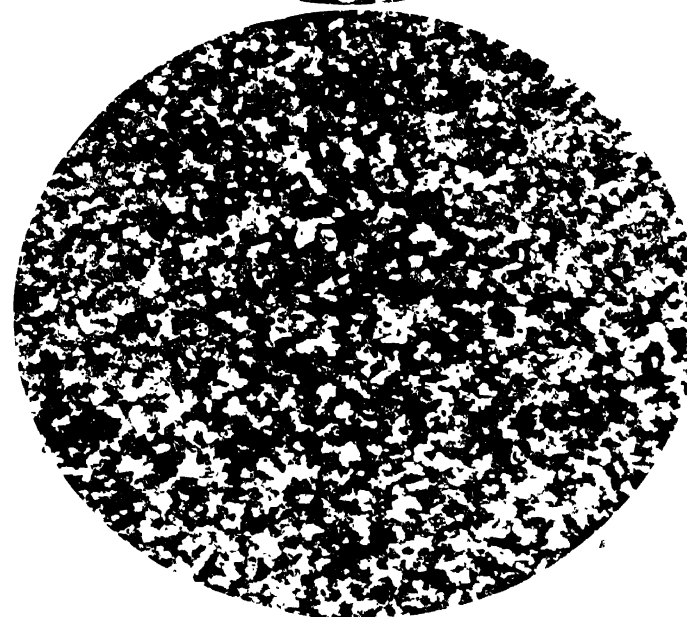
# PLATE 48



X 3

Fig. 100 Cast at 850°

Influence of the temperature of pouring



X 3

Fig. 00 Cast at 700°

1" sand bars of alloy No. 12

# PLATE 49



Fig. 101 Unetched X 100



Fig. 102 HCl + HF etch X 100



Fig. 103 NaOH etch X 100



Fig. 104 HNO<sub>3</sub> etch X 100

round bar of alloy No. 13 sand cast at 850°

# PLATE 50



Fig 105 Unetched X 100



Fig 106 HCl + HF etch X 100



Fig. 107 NaOH etch X 100  
1" round bar of alloy N° 12 cast at 700°

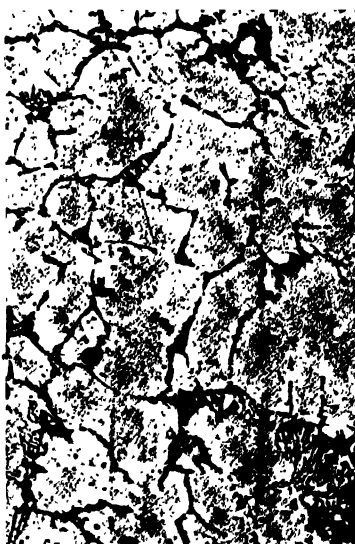
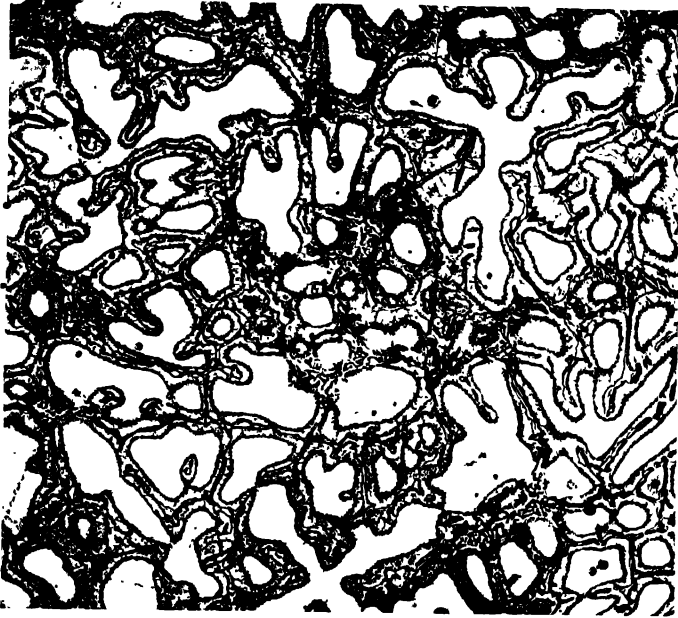


Fig 108 HNO<sub>3</sub> etch X 100

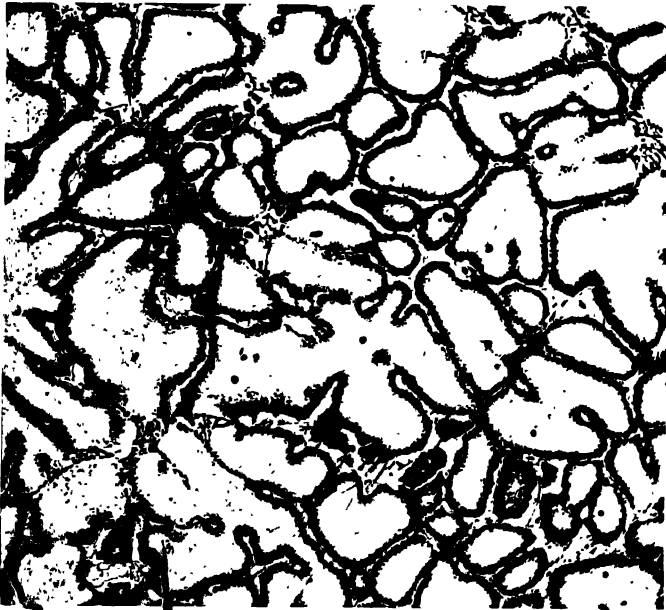
# PLATE 51



X 100

Fig. 110. Cast at 700

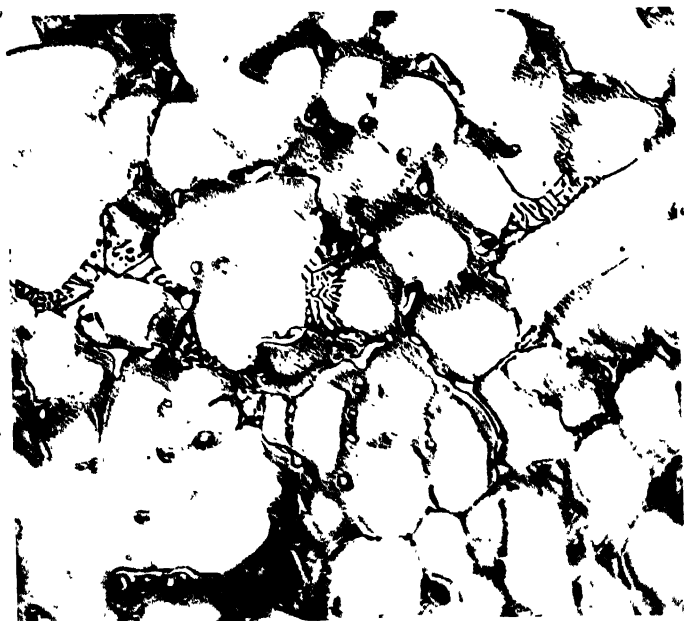
1" round bar of alloy No. 12 (8% Cu, 10% Fe) sand cast, Vilella's etch



X 100

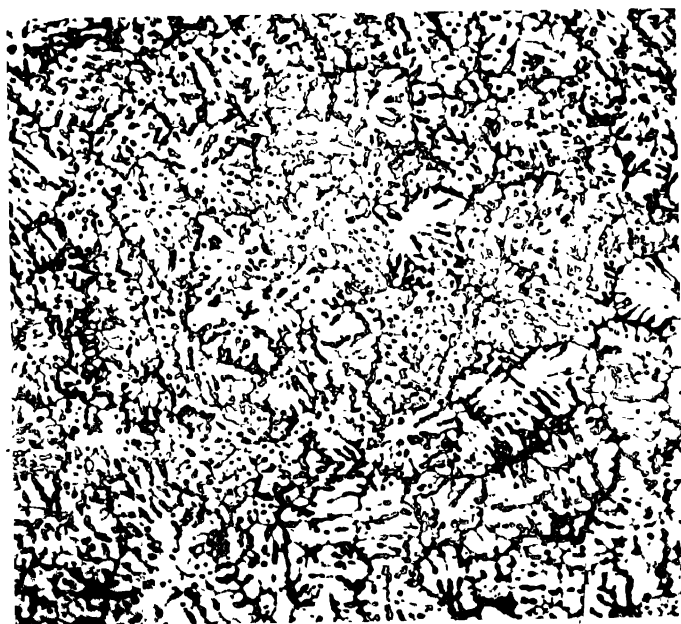
Fig. 100. Cast at 550°

# PLATE 52



X 500

Fig. 112  
Vilella's etch



X 100

Fig. 111

1" roughed bar of alloy N° 12 [8% Cu + 0.8% Fe] chill cast at 675°

# PLATE 53

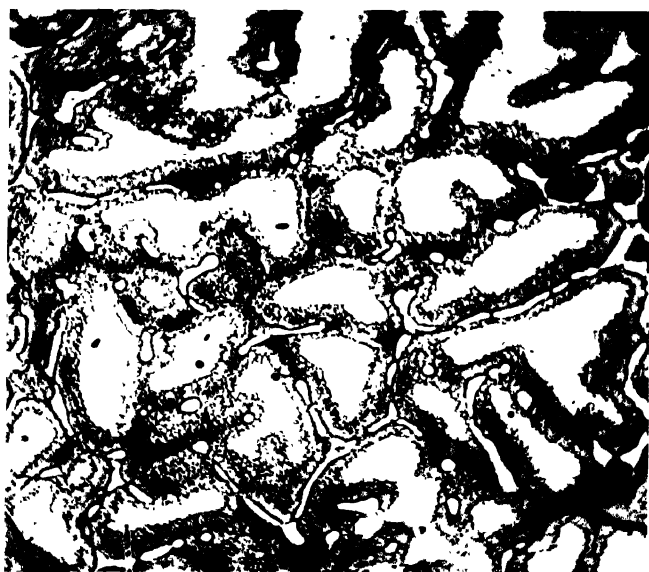


Fig. 113. Cast at 700°C. X 500  
1" round bar of alloy N 12 (8% Cu, 0.8% Fe) chill cast Vilella's etch

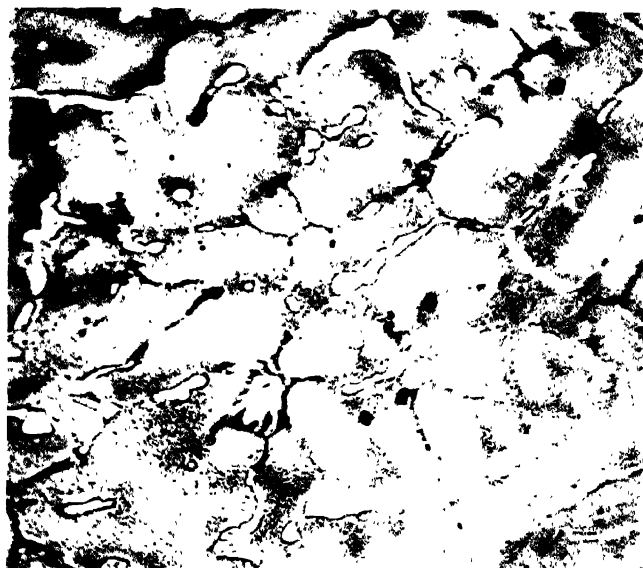


Fig. 114. Cast at 850°C. X 500  
1" round bar of alloy N 12 (8% Cu, 0.8% Fe) chill cast Vilella's etch



PLATE 54

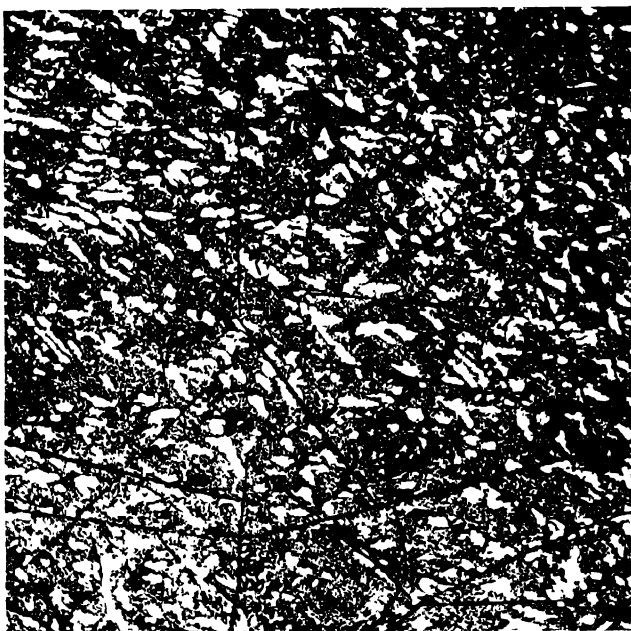


Fig 115 X 100

Chill cast bar of an auxiliary 140' Cu (+ 1.2% Fe) alloy

7

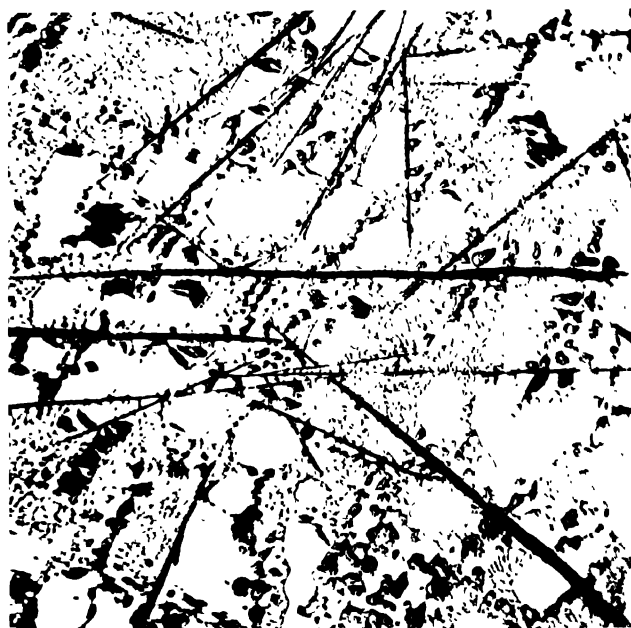


Fig 116

X 500

# PLATE 55

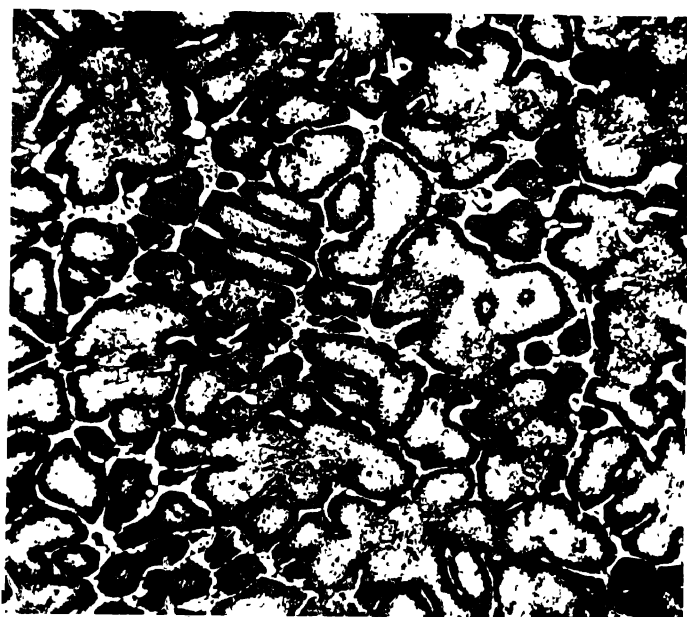


Fig. 117 Dark etched  
1" round bar of 12', Cu  $\pm$  2', Mn  $\pm$  0.8', Fe alloy sand cast at 6-0

X 100

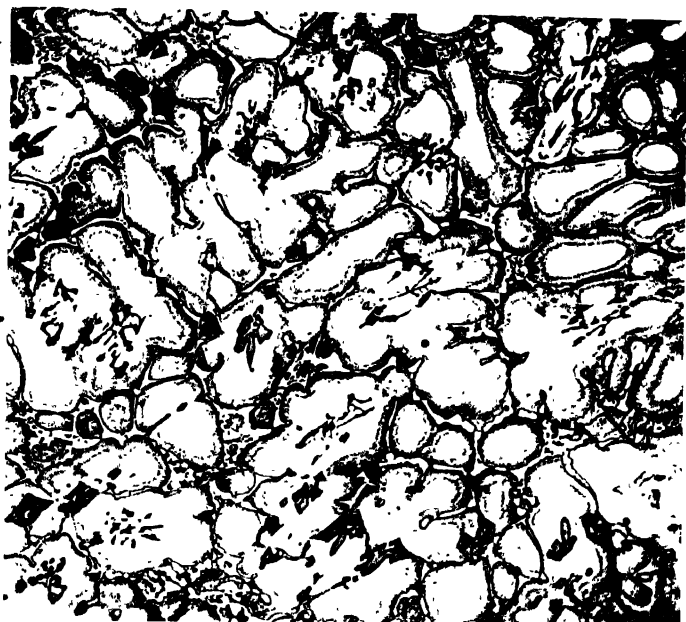


Fig. 118 Light etched

X 100

# PLATE 56



Fig 110 Dark etched  
1" round bar of 12% Cu - 2% Mn - 0.0% Fe alloy, sand cast at 670° X 500



Fig 120 Light etched  
1" round bar of 12% Cu - 2% Mn - 0.0% Fe alloy, sand cast at 670° X 500

PLATE 57



Fig. 121 (top) 10% Cu, 15% Fe alloy, sand cast X 425  
 Fig. 122 (bottom) 12% Zn + 3% Cu (+ 0.8% Fe) alloy sand cast  
 ("Chinese Script") X 425

# PLATE 58

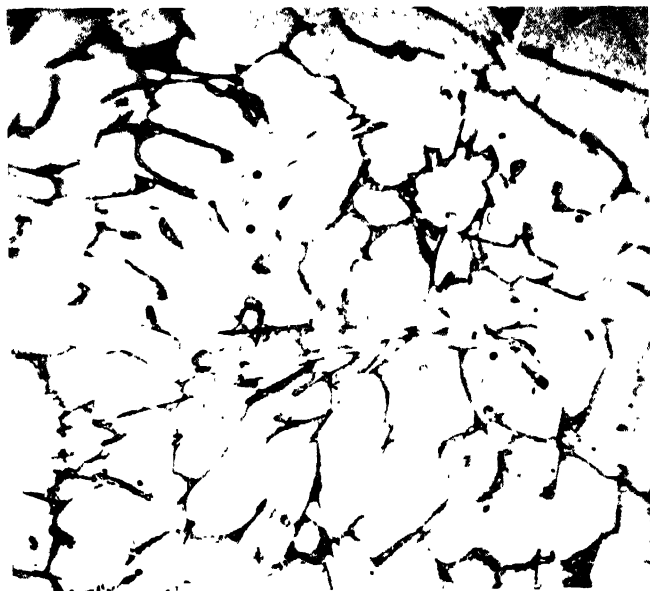


Fig 123 Chill cast  
1" square bar of "Lautal" [4% Cu, 2% Si + (0.7% Fe)]  
X 100

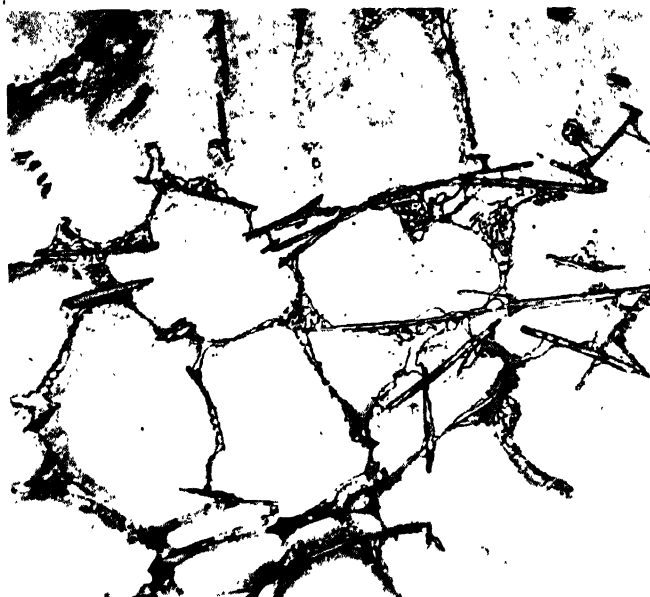


Fig 124 Sand cast  
X 100

PLATE 59



X 500

Fig 126

X 500

Fig 1-5

1" round bar of Lantal (4% Cu, 2% Si + 10% Fe) sand cast

# PLATE 60



Fig 1.7 6 h at 500°, q-d  
Lautal (4% Cu, 2% Si (+ 0.7% Fe))

X 100

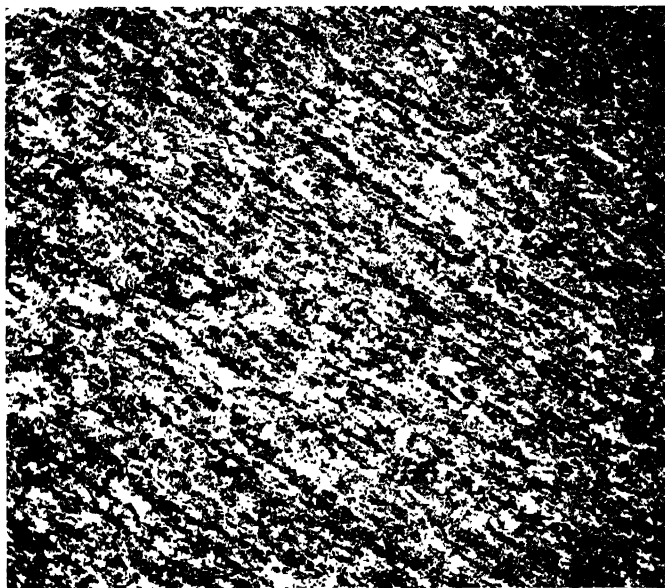


Fig 1.8 6 h at 500°, q-d, 16 h 250°  
forged from 1' sq to 1/2" sq heat treated

X 100

# PLATE 61

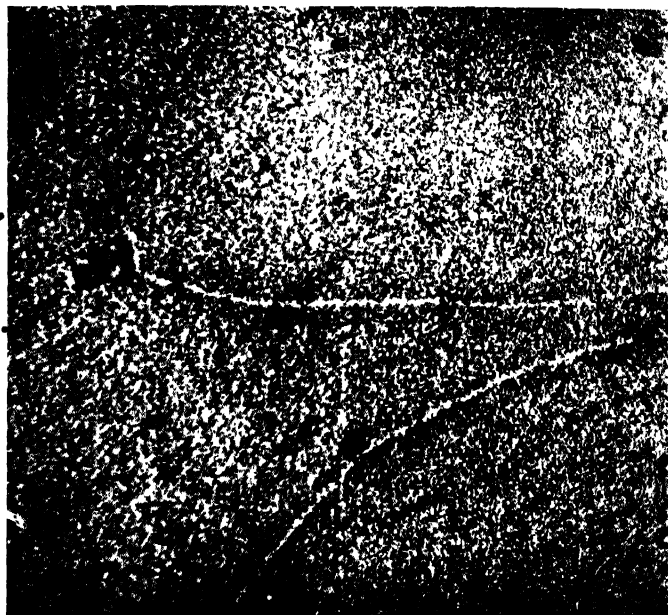


Fig 130 Aludur. chyll cast 12 h 500°, w q-d, 3 h 200° X 500

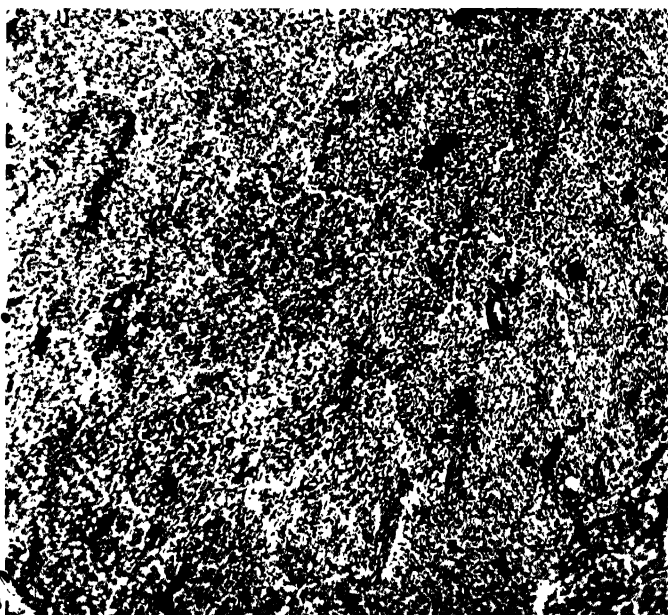
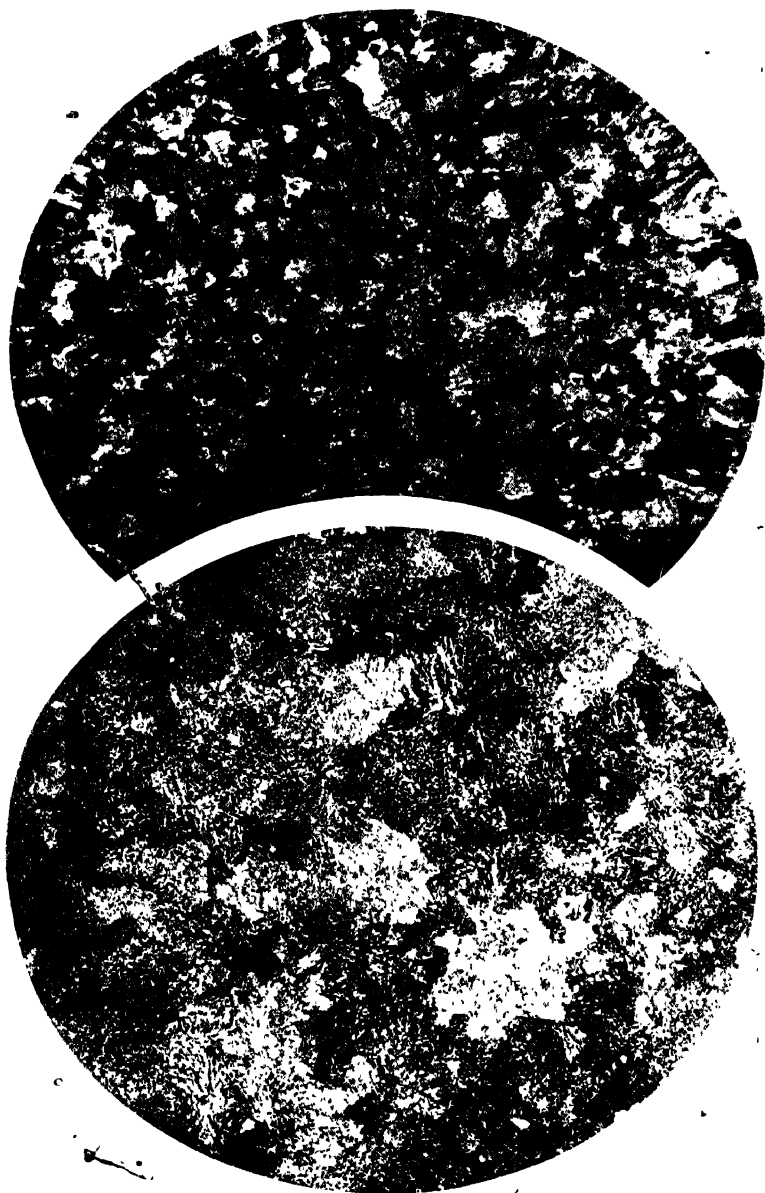


Fig 120 Lantal, forged, 8 h 500°, w q-d, 10 h 250° X 500



PLATE 62



1" round bars of the "Dix" alloy

Fig. 131 (top) Chill cast

Fig. 132 (bottom) Sand cast

$\times 3.5$

$\times 3.5$

# PLATE 63

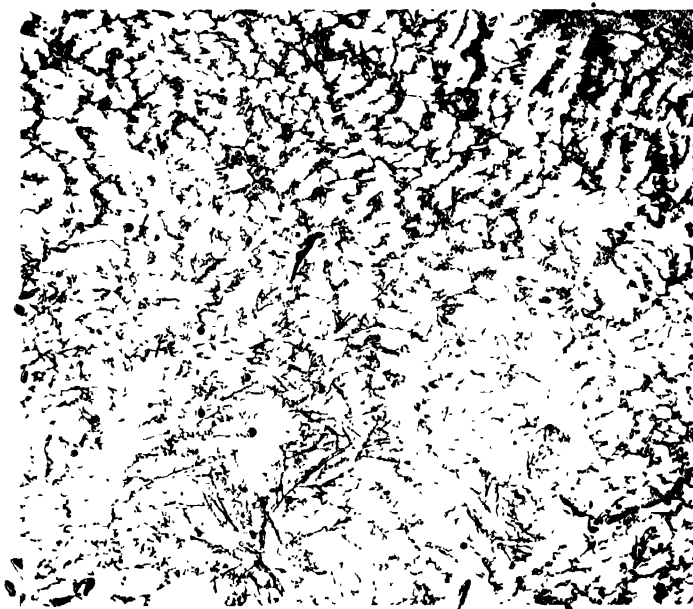


Fig. 133 Chilled cast at 200

X 200

1" round bars of 3% Cu 5% Si 10% Fe (Dux alloy)

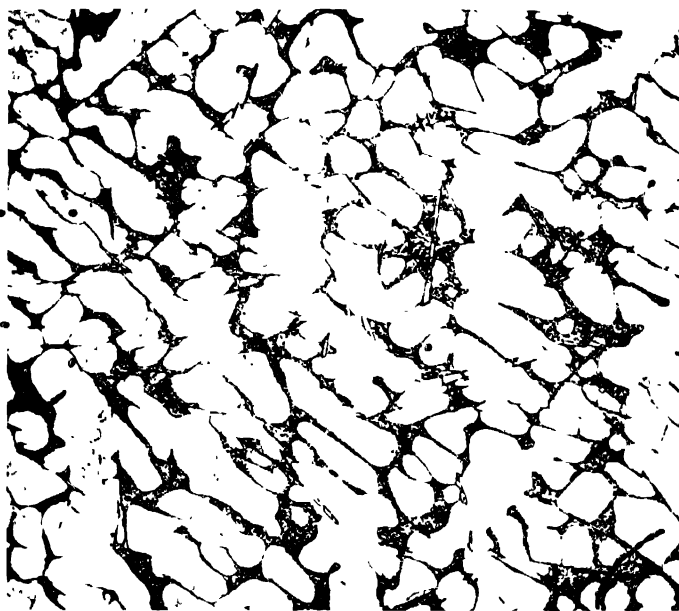


Fig. 134 Sand cast at 100

X 100

PLATE 64

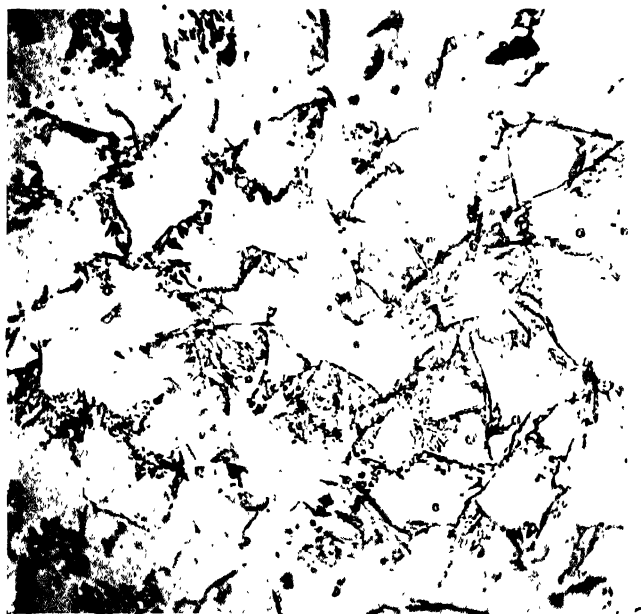


Fig. 135 Chill cast-  
1" round bars of 3% Cu, 5% Si (0.8% Fe) alloy as cast

X 500

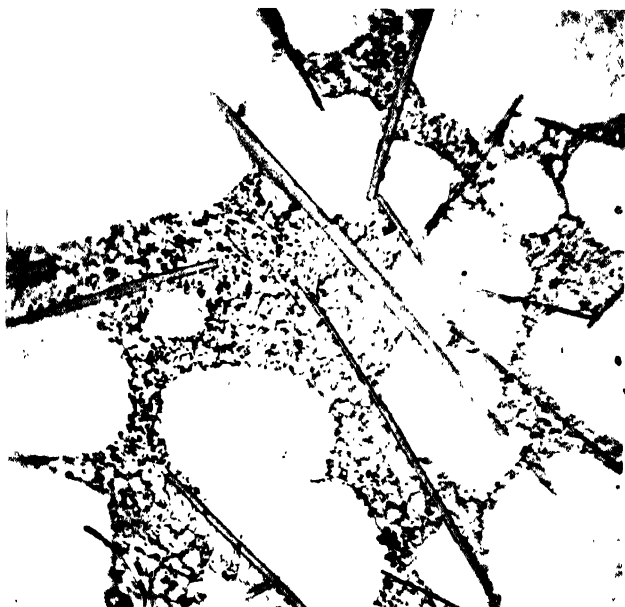


Fig. 136 Sand cast

X 425

PLATE 65

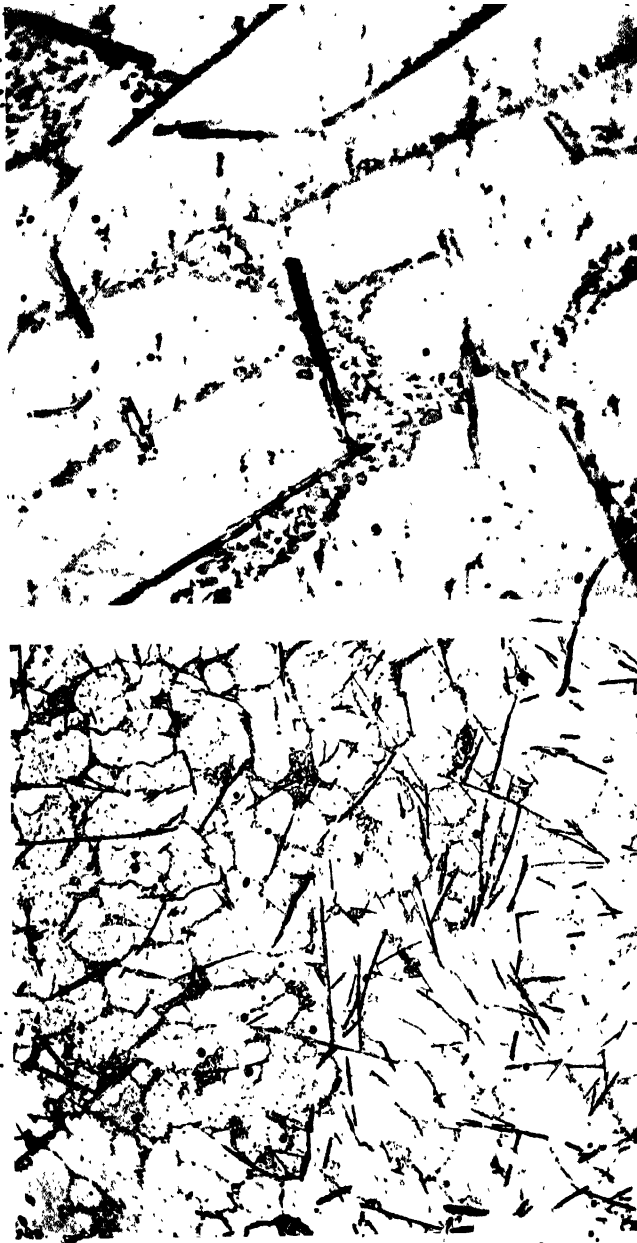


Fig. 137

X 100

1" round bar of 5% Si, 3% Cu ( $\pm 0.8\%$ , Fe) alloy, sand cast, 27 h 480 $^{\circ}$ , w. q-d

Fig. 138

X 500

PLATE 66

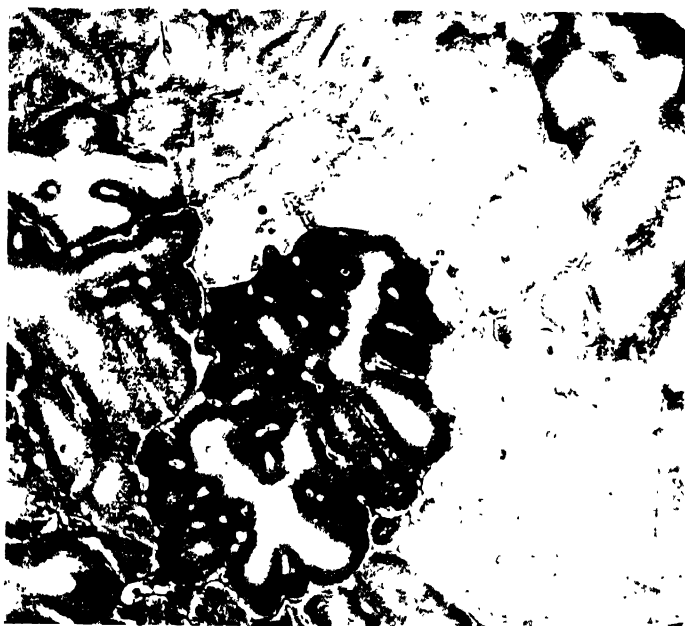


Fig. 30. Sn-11 cast at 700°  
X 100  
1" square bars of 5% Zn (+ 0.2% Pb) alloy.

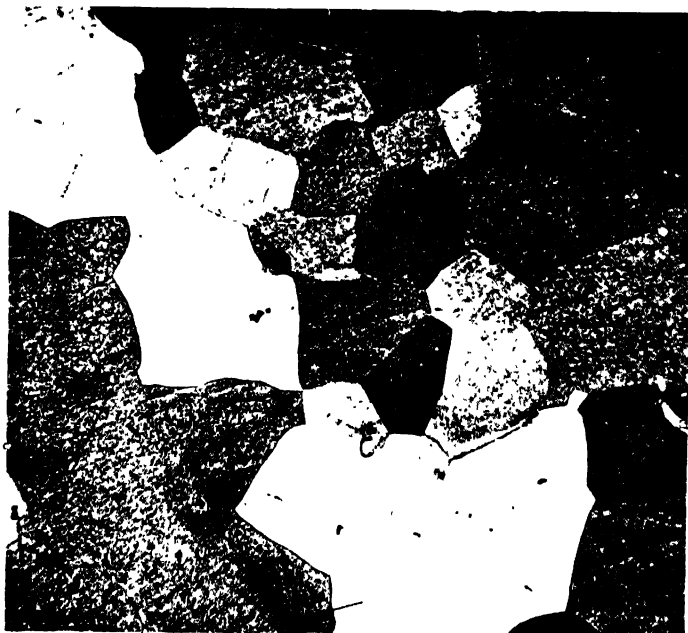
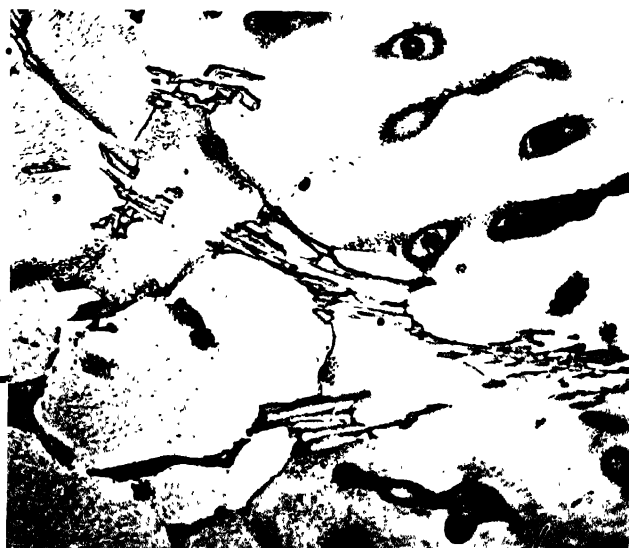


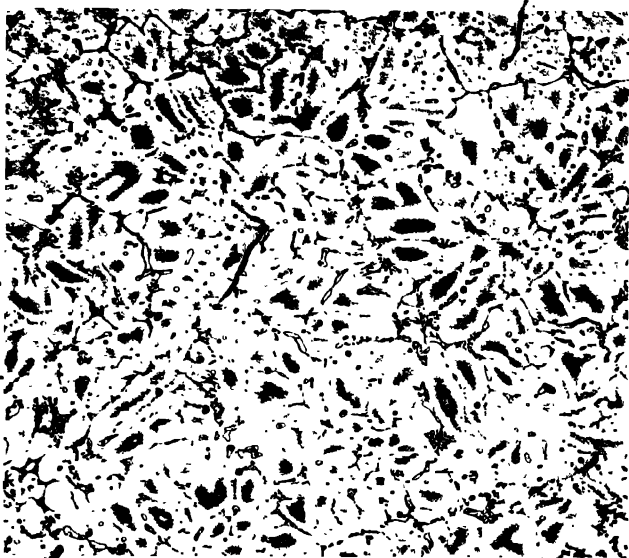
Fig. 140. Same annealed at 300° for 6 h  
X 100

PLATE 67



X 500

Fig 142



X 100

Fig 141

1" square bar of 15% Zn-10% Fe, chill cast at 650°